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GEOCHEMISTRY AND GEOLOGY OF HELIUM

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GEOCHEMISTRY AND GEOLOGY OF HELIUM

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ABSTRACT

Helium is generated by the alpha decay of radioactive nuclides in certain rocks and minerals. Concentration of uranium, which is an alpha emitter, in all the rock types was determined using the gamma ray spectroscopy technique and a 400-Channel Pulse Height Analyzer. This concentration is a measure of helium generating potential due to the uranium content of the specimens examined for gamma radiation. Considering thorium to uranium ratio of 3 to 1, it is suggested that the amount of helium derived from uranium is equal in amount to that generated by thorium. Other alpha emitters such as radium and polonium were not considered because of their extremely low abundances in terrestrial material. It was concluded that the sedimentary rocks, as well as igneous and metamorphic rocks, are potential helium producers.

In addition to major rock types, certain fluids have the ability to dissolve or leach uranium from rocks. These fluids will become alpha emitters after carrying away the radioactive minerals in the rocks. Therefore, there must be a definite relationship between the composition of mobile

ground waters and their content of radioelements. Concentration of the radioelements such as uranium and thorium in fluids is affected by such factors as salinity, temperature, and pressure.

It was found that fluids such as brines and petroleum have the ability to transfer uranium from their original sites. Since the brines and petroleum which are found in rocks today have migrated into their present position, it can be concluded that later migration will partially carry away radioelements like uranium and thorium. Upon entrapment of these alpha emitting fluids, the helium generated by the alpha particles escapes from the solution due to the very insoluble nature of this gas.

Natural gas analyses indicate that there is a good correlation between radiogenic argon and helium. Also, the nitrogen content generally increases with increasing helium content, but this is not always the case. It is concluded that the variable helium content in natural gases is a function of several complex factors and the interaction which takes place among those factors. To name a few of them one could mention the local radioactivity in host rocks, the alpha emitters, preferential retention and diffusion, leakage, solubility, porosity of the host rocks, and the environment containing the host rock.

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CHAPTER I

INTRODUCTION

Statement of the Problem

There are many interesting problems in the geochemistry of rare gases. One general problem is their scarcity in terrestrial materials as compared with their abundance in the solar and stellar atmospheres. Helium is the second most abundant element in the universe after hydrogen, which is the most abundant one. In this research an attempt has been made to explain and account for the cause or causes which may govern this scarcity on earth.

Coexistence of helium with some natural gases presents another geochemical problem. There have been several theories regarding the origin of helium in natural gas. On a broad scale, these theories assume that either: (1) all or part of the helium is radiogenic, which is the helium derived from the disintegration of radionuclides, or (2) it is mostly primordial or the original helium present at the time of the earth's formation which was trapped during the degassing stage of the earth. These theories

have shortcomings, which have been pointed out by many workers (3, 11, 19). An attempt is presented here to postulate a helium generating mechanism to overcome the shortcomings of present theories.

Although a considerable amount of work has been done on the material balance of helium between the earth, the atmosphere and space, little work has been done on the mode of migration of the helium within the earth's crust to the atmosphere. Several possible modes of migration were considered in this work, and a conclusion was made as to which type of migration is the most probable one.

Natural gas analyses from many different areas reveal a wide variation in helium content. As a general rule the helium content increases with increasing nitrogen content. However, there seems to be no definite relationship between helium and nitrogen. An explanation is proposed for the variation of the helium content in natural gas.

Radioactivity of natural environment, host rocks, and certain fluids have a direct bearing on the amount of helium found in source areas. However, assigning the correct relative amount from each contributing source of helium is a very difficult task. The entrapment, escape, retention, and other complex factors may be possible explanations for variation in the helium content of natural gases.

The exact role of communication passages due to such factors as porosity, permeability, and fracture systems is essentially unknown. In this report the individual role of these factors and their importance is considered. Since alpha particles are generally stopped and are converted to helium atoms within a few microns of the surface, fractured basement rocks are good sources of helium. This fracturing creates passageways for the helium which is entrapped in the crystal structure of the rocks to be released. After release, the helium atoms move to the passageways, which are the migratory channels. The channels or fractures are extended through the sedimentary section. And, any helium which is present in the rocks will find its way into the sediments and finally will be partially trapped by suitable geological formations which are impermeable.

Solubility of radioactive minerals such as uraninite (UO_2) in oil and brines is still unknown, however, a favorable solubility factor could count for high helium content in special locations where the helium concentration is about 8 mole percent. It is proposed that circulating or migrating fluids such as ground water or petroleum could partially dissolve the uranium and thorium content of the host rocks and actually become an alpha emitting fluid. Such alpha emitting fluids can be good sources of helium.

Subsequent migration of oil and gas into traps is an acute problem in the geochemistry of helium. The helium generated by uranium and thorium dissolved in petroleum will produce helium within the petroleum and brine fluids. Then the helium by its very insoluble nature may escape from the solution and be trapped with natural gas in the same reservoir.

The Subject of Geochemistry

Geochemistry may be defined as the science concerned with the chemistry of the earth and its component parts. It deals with the distribution and migration of the chemical elements within the earth in space and in time. The main tasks of geochemistry may be summarized as follows:

1. The study of distribution and migration of individual elements in various parts of the earth, and the principles governing this distribution and migration.

2. The determination of relative and absolute abundances of the elements and their isotopes in the earth.

Therefore, studies in the geochemistry and geology of helium should contribute to the environmental control of helium generating and helium bearing rocks.

CHAPTER II

RADIOACTIVITY

Introduction

Atoms have diameters of 10^{-8} cm and are composed of electrons surrounding a central nucleus. The nucleus has a diameter of 10^{-12} cm, and electrons are bound to it by the electrostatic attraction of their negative charge to the positive charge of the nucleus. All nuclei consist of neutrons and protons, two types of particles of nearly equal mass.

The nuclear charge, or atomic number, Z, is the integral number of protons in the nucleus. The total number of neutrons and protons in a nucleus is the mass number A. Nuclei of the same Z but different A are different forms of the same element and are called isotopes. The mass of an electron or a beta particle is only 1/1850 the mass of a proton. When a nucleus decays by beta emission, Z increases by 1 unit, because one negative charge is removed, and A remains essentially constant. Alpha particles are the nuclei of helium $(He)^{++}$, and thus have a mass of 4 atomic mass units and a double positive charge. Therefore, in a

nucleus decaying by alpha emission, Z will decrease by 2 and A by 4.

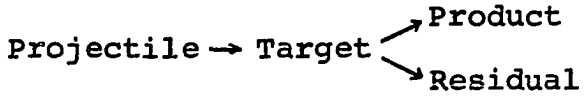
Natural alpha particles usually have energies of several million electron volts (Mev); beta rays range from fractions of an electron volt (ev) to several Mev, and most natural gamma rays have energies of the order of 1 Mev.

Nuclear Reactions

Positively charged particles, such as alphas, experience an electrostatic (Coulomb) repulsion as they approach a nucleus. However, if the projectile particle has sufficient kinetic energy, it penetrates inside the nuclear radius where the strong, short-range, attractive forces are acting. The projectile combines into one body with the target nucleus, forming an excited compound nucleus. In a few shakes, (10^{-12} seconds), the compound nucleus splits into a product particle and a residual nucleus. Such a reaction is usually written as follows:

Target (Projectile, Product) Residual.

or,



The projectile and product particles are commonly abbreviated. For example, the production of protons and carbon^{14} from nitrogen by neutrons in the atmosphere is denoted

$$N^{14}\ (n,p)\ C^{14}$$

or,

$$n \longrightarrow N^{14} \nearrow P \quad \searrow C^{14}$$

If the projectile and product particles are identical, the process is called scattering. The product (scattered) particle always has less energy than projectile.

Radioactive Decay

Radioactive processes are spontaneous nuclear reactions (spontaneous transmutations), characterized by the radiation which is emitted. They occur at random, with a measurable rate, and the exact moment when a given atom will decay cannot be predicted. This spontaneous transmutation will cause a nuclide to convert into another nuclide in an attempt to form a more stable configuration, under release of energy in the form of a different radiation. If the probability of transmutation is nonexistent or small, the nuclide is stable or weakly radioactive, and if it is great, the nuclide is strongly radioactive. If more than one consecutive change occurs before stability is reached, a radioactive chain, or series, is formed. Radioactive nuclides are commonly called radionuclides.

Radioactive disintegration may be treated statistically, and the shape of radicactive decay graphs determined experimentally, as presented in Figure 1, shows that

the activity decreases in an exponential manner. Therefore, the number of a radioactive nuclide to disintegrate, or decay, in a time interval (rate of disintegration) is proportional to the total numbers of atoms of the given nuclide present at that time. Because the disintegration is a continuous process, the number of radioactive atoms will change constantly. The lifetime of a radioactive nucleus may have any value between zero and infinity and is independent of the previous length of life of the nucleus.

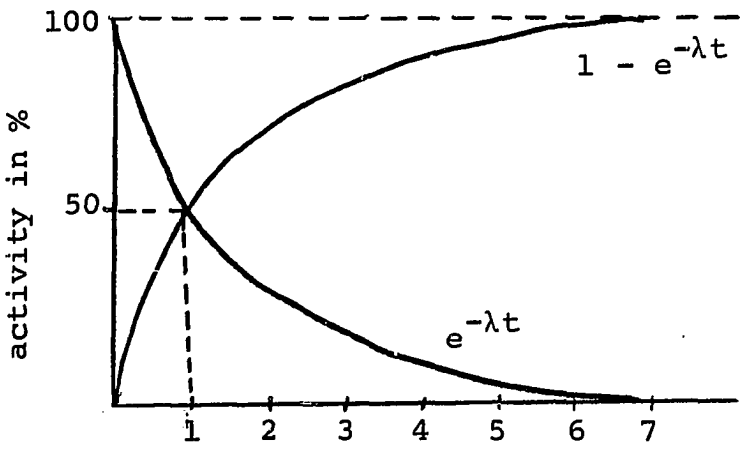


Figure 1. Exponential growth ($1 - e^{-\lambda t}$) and decay ($e^{-\lambda t}$) of a radionuclide.

The fundamental law of radioactive disintegration states that the number of atoms disintegrating per unit time, $-dN/dt$, is proportional to the number of atoms present, N. Consider a group containing a large number (N) of identical radioactive elements. The probability that any particular atom will disintegrate in unit time is λ, the radioactive decay constant. The activity of these atoms, A, i.e., the total number of disintegrations per unit time, will be $N\lambda$. The rate of depletion, dN/dt, of the group of atoms is equal to the activity. Therefore, the activity of the parent element is proportional to the number of parent atoms decaying in a unit time. Also, the number of parent atoms decaying per unit time is proportional to the number of parent atoms present. This constant of proportionality is called the decay constant. These assumptions may be expressed mathematically as

$$dN/dt = -N\lambda \quad (a); \qquad A = K\,(-dN/dt) \quad (b) \qquad (1)$$

where A is the activity of the parent element, t is the time, and K is a constant. Because N decreases as time increases, insert a minus sign in Equation (1a). Rewriting Equation (1a) in integral form, with the variable separated,

$$\int dN/N = -\int \lambda dt \quad (a); \quad \text{or} \quad dN/dt = -\lambda N \quad (b) \quad (2)$$

Let's now make the fundamental assumption that the probability of decay of an atom is independent of the age

of that atom. Then if λ is independent of t and is constant, and characterizes the atomic species in question, one can integrate Equation (2a),

$$\ln N = -\lambda t + C \tag{3}$$

If there were N_o atoms at t = o, while N atoms remain at time t = t, then $\ln N = \ln N_o = C$, and Equation (3) becomes

$$\ln (N/N_o) = -\lambda t$$

or, in the usual exponential form,

$$N = N_o e^{-\lambda dt} \tag{4}$$

This exponential relation represents the decay derived experimentally and illustrated by Figure 1. The constant λ with dimension of 1/sec was originally called the radioactive constant, but is now called the disintegration constant or decay constant of the radioactive nuclide. It is a definite and specific property of the radionuclide, usually independent of the chemical state and the conventional physical conditions may be temperature, pressure, concentration, or age of the radioactive atoms.

The disintegration law of Equation (4) applies universally to all radioactive nuclides, but the constant λ is different for each nuclide. The known radioactive nuclide extends between $\lambda = 3 \times 10^6$ per second for thorium C'

and $\lambda = 1.58 \times 10^{-18}$ per second for thorium. Among the more than 800 known radioactive nuclides, no two have exactly the same decay constant. The identification of some radioactive samples can be made simply by measuring λ, which can serve as a type of qualitative chemical analysis.

Because radioactive decay is treated as a statistical process in which λ represents the probability that an atom will disintegrate in a unit time, it is evident that fluctuations will occur in the observed number of disintegrations per unit time. These fluctuations become more prominent as a smaller number of disintegration atoms are actually observed.

Units of Radioactivity

The Curie unit was redefined in 1950 (Evans, 1955) by action of the International Joint Commission on Standards, Units and Constants of Radioactivity. This definition is "The Curie is a unit of radioactivity defined as the quantity of any radioactive nuclide in which the number of disintegration per second is 3.70×10^{10}." The number of disintegrations is the sum of all competing modes of disintegration. Therefore, the full decay scheme of a nuclide has to be known before the quantity of any sample can be expressed in Curies as a result of measurements on any particular mode of disintegration, such as α or β rays. In

practical use, the quantity of any radionuclide is usually nearly synonymous with the total activity of the nuclide (Evans, 1955).

Thus, a Curie of radium^{226} is approximately 1 gram; a Curie of radon^{222} is 0.66 cubic mm at standard temperature and pressure; and a Curie of uranium^{238} is about 3000 kg.

Half Life and Mean Life

The half life, T, of an element is the time period over which the chance of survival of a particular radioactive atom is exactly one half, or, the length of time required for one half of a given number of atoms to decay. Therefore, if T is the half life of the radionuclide,

$$N_o/2 = N_o e^{-\lambda T}$$

Where: e = 2.7182

ln = natural logarithm

from which

$$T = \ln 2/\lambda = 0.693/\lambda$$

In a large initial stock of N_o atoms, with initial activity $N_o\lambda$, the expectation value of the activity $N\lambda$, one half time later, is $N\lambda = N_o\lambda/2$.

The actual life of any particular atom can have any value between zero and infinity. The average life of a

large number of atoms is a definite quantity. It can be found by adding the lifetimes of all atoms and dividing by the total number of atoms,

$$\tau = \frac{1}{N_o} \int_{N_o}^{o} t(-dN) = \frac{1}{N_o} \int_{o}^{\infty} t(-dN/dt)\, dt$$

$$= \frac{1}{N_o} \int_{o}^{\infty} t\lambda N_o e^{-\lambda t} dt = \lambda \int_{o}^{\infty} te^{-\lambda t}\, dt$$

$$\tau = 1/\lambda$$

It is seen that the average or mean life of an atom is not the same as the half life of an element, but instead is reciprocal of the decay constant of the element.

The following mutual relationships exist between the constants T, λ, and τ:

$$\lambda = 1\tau = 0.69315/T$$

$$\tau = 1/\lambda = T/0.69315 = 1.442T$$

$$T = 0.69315/\lambda = 0.69315\tau$$

The relationship between T and τ is shown graphically in Figure 2.

Radioactive Equilibrium

If a system contains both the decaying parent and its daughter, two general cases may be distinguished depending on the relationship between the half-lives of the two nuclides:

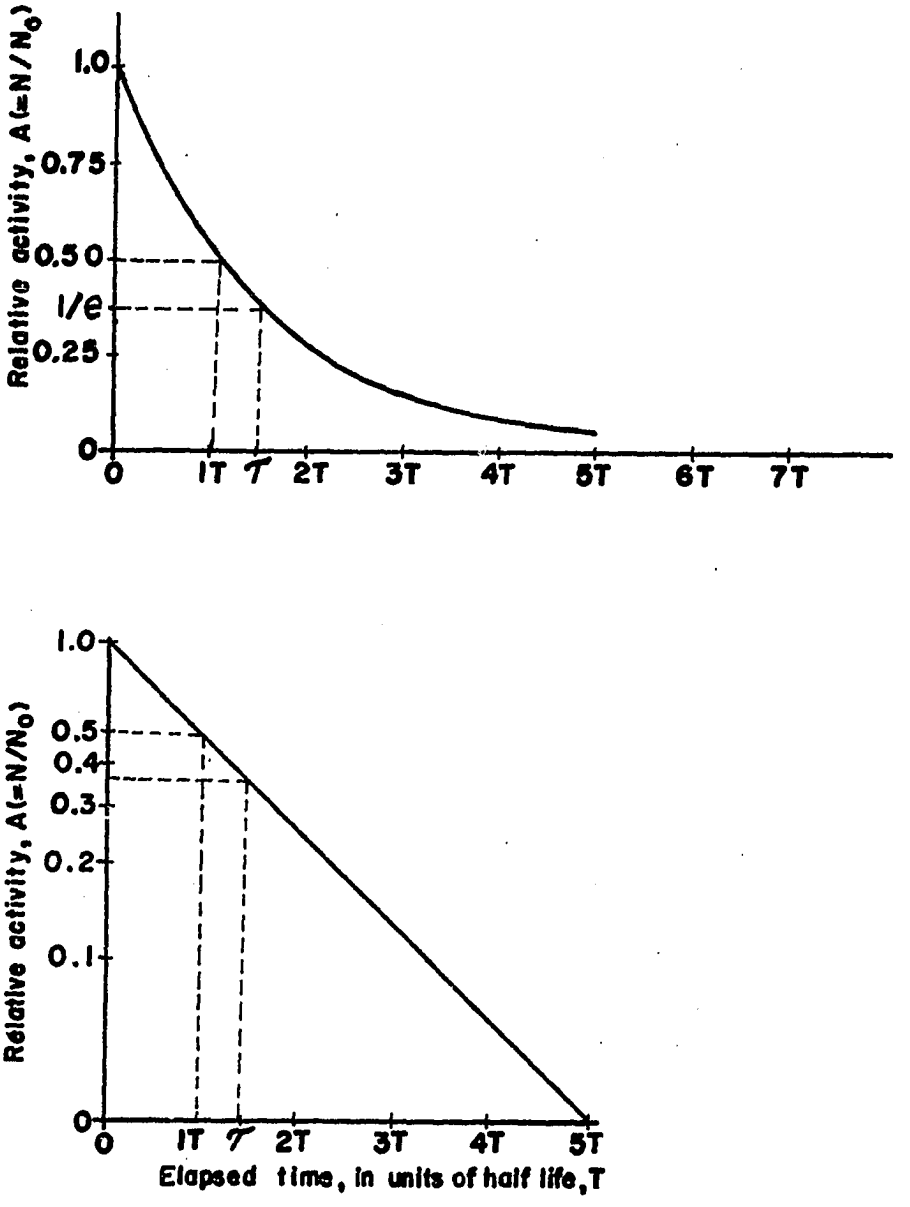


Figure 2. Radioactive decay curves, showing relative activity as a function of elapsed time. The upper curve is plotted on linear coordinates while lower is plotted on semi-log paper.

(1) In a case where the parent is shorter lived than the daughter, $\lambda_1 > \lambda_2$, where λ_1 and λ_2 are the decay constants of the parent and the daughter respectively. If the parent was initially free of the daughter, the amount of the daughter will increase, pass through a maximum, and then decrease. In this case no steady state is attained between the amounts of the parent and the daughter at any time.

(2) If the parent is longer lived than the daughter, $\lambda_1 < \lambda_2$, and a steady state, called radioactive equilibrium, will eventually be reached. This will happen when the rate of decay of the daughter is as rapid as the rate of its formation from the parent. When this happens, the N_1/N_2 ratio and the ratio of the disintegration rates of the parent and the daughter become constant. N_1 and N_2 are referred to as the number of atoms of the parent and daughter, respectively, that are present at a time, t.

The rate of decay of the parent, obtained from general radioactive decay equation (Eq. 4), is equal to $\lambda_1 N_1$ and the rate of decay of the daughter is $\lambda_2 N_2$. For steady state, when the rate of formation of the daughter equals the rate of its own disintegration, one can write, $\lambda_1 N_1 = \lambda_2 N_2$ or, by substituting the half-lives, T_1 and T_2, of the parent and the daughter, respectively, $N_1/T_1 = N_2/T_2$.

Because in the case examined, the daughter also disintegrates, it will be the parent of a new daughter

which, if active, the rate of decay is $\lambda_3 N_3$. Consequently, in equilibrium for a general case, when there are several successive members of a radioactive series, equilibrium condition becomes,

$$\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3 = \ldots$$

Radioactive Nuclides

There are about sixty naturally occurring radioactive nuclides. More than a thousand species (Rankama, 1954) have been already prepared artificially in various nuclear transmutations and disintegration processes from naturally stable nuclides. In fact, virtually every known element and several previously unknown elements have been produced in radioactive forms.

There are several kinds of radiations that are emitted from radioactive nuclei during their decay. Most radioactive nuclides found in nature are either alpha or beta emitters, and their radiation often is accomplished through gamma ray radiation. In this paper only alpha radiation will be considered because of its importance in the generation of helium.

Alpha-Radioactivity

Systematics of Alpha Emitters

Alpha decay is energetically possible in all the members of the whole upper third of the periodic system.

It becomes prominent in the nuclide region above Z 82 (lead). For most heavy radionuclides above A 212, systematic trends in the alpha decay properties indicate that at constant Z, the alpha disintegration energy decreases (Rankama, 1963). All elements with Z greater than 80 found in nature have radioactive isotopes, and above Z 82 no stable elements exist. Consequently the alpha half life increases with increasing A, in a nearly linear fashion.

The alpha half lives depend prominently to a marked degree on the alpha decay energies. Only when the alpha decay energy exceeds a certain value does the alpha lifetime become short enough to be detectable. The limiting energy value depends on Z. Thus, the energy required for a half life of 10^{-12} years increases from approximately 2 Mev at Z 62 (samarium) to approximately 4 Mev around Z 92 (uranium). In the transuranium range, increase of the energy from 4 Mev to 8 Mev decreases the alpha half life by a factor greater than 10^{20}. The investigation of the collateral radioactive series, transuranium elements, and neutron deficient heavy elements, has revealed the existence of approximately 70 new alpha emitters as contrasted with only 29 alpha active nuclides known to exist in nature (Rankama, 1954).

The alpha half lives decrease gradually from 1.39×10^{10} years for Th^{232} to hours (h) and minutes (m) for the

heaviest nuclides. Among the heavy nuclides, several with a relatively low A value decay by an orbital-electron capture that often competes with alpha disintegration. Table 1 shows different radionuclides, their manner of decay, decay product, and their half lives.

Range and Absorption of Alpha-Particles

Most of the alpha particles emitted from a radioactive source have very nearly straight-lined tracks of identical length (Howard, 1963). Over their tracks they are capable of ionizing the matter that they traverse. The length of track is called the range of the alpha particles. The range is defined as the distance in dry air at standard conditions, travelled by the alphas from their source to a point at which they no longer produce ionization. At this point the alpha particle is converted to a molecule of helium gas.

Because energy is consumed during ionization, the velocity of an alpha particle will decrease toward the end of its track. The mean range of an alpha particle passing through air, R, is listed in Table 2 which is based on data from Rankama (1954).

TABLE 1

NATURAL RADIONUCLIDES

Single Primary Radionuclides

Parent Nuclide				Decay Product			
Atomic Number	Element	Mass Number	Manner of Decay	Atomic Number	Element	Mass Number	Half Life
0	neutron	1	beta -	1	H	1	12.8 m
19	K	40	89% beta -	20	Ca	40	
			11% K cap	18	Ar	40	1.3×10^{9} y
23	V	50	K cap	22	Ti	50	4×10^{14} y
37	Rb	87	beta -	38	Sr	87	5.0×10^{10} y
49	In	115	beta -	50	Sn	115	6×10^{14} y
57	La	138	70% K,L cap	56	Ba	138	
			30% beta -	58	Ce	138	1.0×10^{11} y
58	Ce	142	alpha	56	Ba	138	5.1×10^{15} y
60	Nd	144	alpha	58	Ce	140	2.2×10^{15} y
62	Sm	147	alpha	60	Nd	143	1.25×10^{11} y
71	Lu	176	beta -	72	Hf	176	2.4×10^{10} y
73	Ta	180	beta - (?)	74	W	180	more than 10^{12} y
74	W	180(?)	alpha	72(?)	Hf(?)	176(?)	long
75	Re	187	beta -	76	Os	187	8×10^{10} y
78	Pt	190	alpha	76	Os	186	5.9×10^{11} y
78	Pt	192	alpha	76	Os	188	10^{15} y
83	Bi	209	alpha	81	Tl	205	2×10^{17} or more than 2×10^{18} y

TABLE 1 (Continued)

Radioactive Families
The U^{238} (Uranium) Family

Parent Nuclide				Decay Product			
Atomic Number	Element	Mass Number	Manner of Decay	Atomic Number	Element	Mass Number	Half Life
92	U	238	alpha	90	Th	234	4.51×10^9 y
90	Th	234	beta -	91	Pa	234	24.10 d
91	Pa	234	beta -	92	U	234	1.175 m & 6.66 h
92	U	234	alpha	90	Th	230	2.48×10^5 y
90	Th	230	alpha	88	Ra	226	8.0×10^4 y
88	Ra	226	alpha	86	Rn	222	1622 y
86	Rn	222	alpha	84	Po	218	3.8229 d
84	Po	218	99.98% alpha	82	Pb	214	
			0.02% beta -	85	At	218	3.05 m
82	Pb	214	beta -	83	Bi	214	26.8 m
85	At	218	99.9% alpha	83	Bi	214	
			0.1% beta -	86	Rn	218	1.5 to 2 s
83	Bi	214	0.04% alpha	81	Tl	210	
			99.96% beta -	84	Po	214	19.7 m
86	Rn	218	alpha	84	Po	214	0.019 s
84	Po	214	alpha	82	Pb	210	1.64×10^{-4} s
81	Tl	210	beta -	82	Pb	210	1.32 m
82	Pb	210	beta -	83	Bi	210	19.4 y
83	Bi	210	99+% beta -	84	Po	210	
			5×10^{-5}% alpha	81	Tl	206	5.013 d
81	Tl	206	beta -	82	Pb	206	4.19 m
84	Po	210	alpha	82	Pb	206	138.401 d
82	Pb	206	STABLE				

TABLE 1 (Continued)

Radioactive Families
The Th^{232} (Thorium) Family

Parent Nuclide				Decay Product			
Atomic Number	Element	Mass Number	Manner of Decay	Atomic Number	Element	Mass Number	Half Life
90	Th	232	alpha	88	Ra	228	1.39×10^{10} y
88	Ra	228	beta -	89	Ac	228	6.7 y
89	Ac	228	beta -	90	Th	228	6.13 h
90	Th	228	alpha	88	Ra	224	1.910 y
88	Ra	224	alpha	86	Rn	220	3.64 d
86	Rn	220	alpha	84	Po	216	51.5 s
84	Po	216	alpha	82	Pb	212	0.158 s
82	Pb	212	beta -	83	Bi	212	10.64 h
83	Bi	212	63.8% beta -	84	Po	212	
			36.2% alpha	81	Tl	208	60.5 m
81	Tl	208	beta -	82	Pb	208	3.10 m
84	Po	212	alpha	82	Pb	208	3.04×10^{-7} s
82	Pb	208	STABLE				

TABLE 1 (Continued)

Radioactive Families

The U^{235} (Actinium) Family

Parent Nuclide				Decay Product			
Atomic Number	Element	Mass Number	Manner of Decay	Atomic Number	Element	Mass Number	Half Life
92	U	235	alpha	90	Th	231	7.1×10^8 y
90	Th	231	beta -	91	Pa	231	25.64 h
91	Pa	231	alpha	89	Ac	227	3.43×10^4 y
89	Ac	227	98.8% beta -	90	Th	227	
			1.2% alpha	87	Fr	223	21.6 y
87	Fr	223	99+% beta -	88	Ra	223	
			6×10^{-3}% alpha	85	At	219	22 m
90	Th	227	alpha	88	Ra	223	18.17 d
88	Ra	223	alpha	86	Rn	219	11.68 d
85	At	219	3% beta -	86	Rn	219	
			97% alpha	83	Bi	215	0.9 m
83	Bi	215	beta -	84	Po	215	8 m
86	Rn	219	alpha	84	Po	215	3.92 s
84	Po	215	99+% alpha	82	Pb	211	
			5×10^{-4}% beta -	85	At	215	1.83×10^{-3} s
85	At	215	alpha	83	Bi	211	10^{-4} s
82	Pb	211	beta -	83	Bi	211	36.1 m
83	Bi	211	99.7% alpha	81	Tl	207	
			0.3% beta -	84	Po	211	2.16 m
84	Po	211	alpha	82	Pb	207	0.52 s
81	Tl	207	beta -	82	Pb	207	4.79 m
82	Pb	207	STABLE				

TABLE 1 (Continued)

Radioactive Families

The U^{237} (Neptunium) Family

Parent Nuclide				Decay Product			
Atomic Number	Element	Mass Number	Manner of Decay	Atomic Number	Element	Mass Number	Half Life
92	U	237	beta -	93	Np	237	6.75 d
93	Np	237	alpha	91	Pa	233	2.20×10^{6} y
91	Pa	233	beta -	92	U	233	27.0 d
92	U	233	alpha	90	Th	229	1.62×10^{5} y
90	Th	229	alpha	88	Ra	225	7340 y
88	Ra	225	beta -	89	Ac	225	14.8 d
89	Ac	225	alpha	87	Fr	221	10.0 d
87	Fr	221	alpha	85	At	217	418 m
85	At	217	alpha	83	Bi	213	0.018 s
83	Bi	213	98% beta -	84	Po	213	
			2% alpha	81	Tl	209	47 m
81	Tl	209	beta -	82	Pb	209	2.2 m
84	Po	213	alpha	82	Pb	209	4.2×10^{-6} s
82	Pb	209	beta -	83	Bi	209	3.30 h
83	Bi	209	alpha(?)	81	Tl	205	2×10^{17} y, or more than 2×10^{18} y
81	Tl	205	STABLE				

TABLE 1 (Continued)

Induced Radionuclides

Cosmogenic Radionuclides Formed in Meteorites

Parent Nuclide				Decay Product			
Atomic Number	Element	Mass Number	Manner of Decay	Atomic Number	Element	Mass Number	Half Life
1	T(H)	3	beta -	2	He	3	12.26 y
4	Be	7	K cap	3	Li	7	53.6 d
4	Be	10	beta -	5	B	10	2.5×10^6 y
6	C	14	beta -	7	N	14	5568 y
9	F	20	beta -	10	Ne	20	11 s
9	F	21	beta -	10	Ne	21	5 s
10	Ne	19	beta +	9	F	19	18.5 s
10	Ne	23	beta -	11	Na	23	40 s
11	Na	20	beta +	10	Ne	20	0.3 s
11	Na	21	beta +	10	Ne	21	23 s
11	Na	22	beta +, K cap	10	Ne	22	2.58 y
13	Al	26	beta +	12	Mg	26	8×10^5 y
14	Si	32	beta -	15	P	32	710 y
15	P	32	beta -	16	S	32	14.22 d
15	P	33	beta -	16	S	33	24.4 d
16	S	35	beta -	17	Cl	35	87 d
17	Cl	36	beta -	18	Ar	36	3.08×10^5 y
18	Ar	39	beta -	19	K	39	265 y
19	K	40	beta -, K cap	20,18	Ca, Ar	40	1.3×10^9 y
20	Ca	41	K cap	19	K	41	1.1×10^5 y
22	Ti	44	K cap	21	Sc	44	approx. 10^3 y
25	Mn	53	K cap	24	Cr	53	approx. 10^6 y
28	Ni	59	K cap	27	Co	59	8×10^4 y

TABLE 1 (Continued)

Induced Radionuclides

Cosmogenic Radionuclides Formed in the Atmosphere

Parent Nuclide				Decay Product			
Atomic Number	Element	Mass Number	Manner of Decay	Atomic Number	Element	Mass Number	Half Life
1	T(H)	3	beta -	2	He	3	12.26 y
4	Be	7	K cap	3	Li	7	53.6 d
4	Be	10	beta -	5	B	10	2.5×10^6 y
6	C	14	beta -	7	N	14	5568 y
11	Na	22	beta +, K cap	10	Ne	22	2.58 y
15	P	32	beta -	16	S	32	14.22 d
15	P	33	beta -	16	S	33	24.4 d
16	S	35	beta -	17	Cl	35	87 d
17	Cl	34	beta +	16	S	34	32.4 m(?)
17	Cl	38	beta -	18	Ar	38	37.3 m(?)
17	Cl	39	beta -	18	Ar	39	55.5 m

Cosmogenic Radionuclides Formed in the Hydrosphere

1	T(H)	3	beta -	2	He	3	12.26 y
17	Cl	36	beta -	18	Ar	36	3.08×10^5 y

Cosmogenic Radionuclides Formed in the Lithosphere

17	Cl	36	beta -	18	Ar	36	3.08×10^5 y

TABLE 1 (Continued)

Induced Radionuclides

Fissiogenic Radionuclides (Formed Mainly in Uranium Minerals)

Parent Nuclide				Decay Product			
Atomic Number	Element	Mass Number	Manner of Decay	Atomic Number	Element	Mass Number	Half Life
1	T(H)	3	beta -	2	He	3	12.26 y
4	Be	8	beta +	3	Li	8	0.5 s
11	Na	22	beta +, K cap	10	Ne	22	2.58 y
17	Cl	36	beta -	18	Ar	36	3.08×10^5 y
38	Sr	89	beta -	39	Y	89	50.5 d
38	Sr	90	beta -	39	Y	90	27.7 y
43	Tc	99	beta -	44	Ru	99	2.12×10^5 y
53	I	129	beta -	54	Xe	129	1.56×10^7 y
53	I	131	beta -	54	Xe	131	8.05 d
53	I	132	beta -	54	Xe	132	2.3 h
53	I	133	beta -	54	Xe	133	21 h
53	I	134	beta -	54	Xe	134	52 m
53	I	135	beta -	54	Xe	135	6.7 h
56	Ba	140	beta -	57	La	140	12.8 d
61	Pm	147	beta -	62	Sm	147	2.6 y

After Goldman, D. T., (1965) and Rankama, K. (1963).

TABLE 2

MEAN RANGE, R, OF ALPHA PARTICLES IN DRY AIR AT 15°C AND 1 ATM. FOR THE NATURAL ALPHA EMITTERS

Uranium Family	R, cm	Actinium Family	R, cm	Thorium Family	R, cm
U^{238}	2.65	U^{235}	2.82	Th^{232}	2.60
U^{234}	3.21	Th^{227}	4.60	Th^{228}	4.00
Th^{230}	3.11	Ra^{223}	4.29	Ra^{224}	4.30
Ra^{226}	3.30	Po^{215}	6.46	Po^{216}	5.64
Po^{210}	3.84	Bi^{211}	5.36	Bi^{212}	4.73

A comparison of the half life values of Table 1 with the range of alpha particles emitted from radionuclides reveals that an inverse relationship exists between the half life and the range of the alpha particles they emit. In gaseous media, the range of an alpha particle depends on the nature of the medium through which it travels, while in solids, its range is of the order of a few hundredths of a mm. The relation of the range of an alpha particle in air to its range in the medium investigated yields a quantity called the relative stopping power of the medium. The range of alpha particles in solids may be estimated by means of an empirical rule formulated by Bragg and Kleeman (Faul, 1954). This equation gives the relation between range in air and the length of path L in any particular medium.

$$L = R(\rho_a/\rho)\sqrt{A/A_a} = 3.2 \times 10^{-4}\ (R/\rho)\sqrt{A}$$

where R is the range in air, ρ_a is the density of air, ρ is the density of the particular medium, A_a is the mean mass number of air, and A is the mean mass number of the medium.

Energy of Alpha-Particles

All the alpha particles emitted from a source may have the same initial velocity, which is of the order of 10^9 cm per second, and consequently all have the same energy. Such alpha particles are monoenergetic. Several emitters, however, produce alpha particle groups of slightly different energies.

Although alpha particles carry considerable energy, they are large and their penetrating power is low. The energy of alpha particles from natural sources varies from 2.14 Mev for Sm^{147} to 10.53 Mev for Po^{212}. A thin sheet of paper will stop most alpha particles, and when a rock or mineral specimen is examined for alpha activity, only the very thin surface layer (about 30 microns) is effective.

CHAPTER III

ORIGIN AND ABUNDANCE OF ELEMENTS

Origin of the Elements

The question of the origin of the elements and their isotopes, of which the matter of the universe is constituted, is one of the most ancient problems in science. Accompanying the gradual improvement of nuclear experimental data, the quantity and the quality of theories of the origin of the elements have advanced markedly (Evans, 1955). The structure of the nuclei of the elements as aggregates of protons and neutrons has resulted in theories to explain their origin and their relative abundances by a synthesis, or buildup. These theories postulate that the nucleus built up starting with either or both of the basic building blocks, which are protons and neutrons. An alternative which has been suggested is that nuclei now in existence resulted from the breakup of a primordial nuclear fluid, with fission and evaporation processes playing a leading role.

The synthesis point of view starts with protons and/or neutrons, but does not attempt an answer to the

perhaps even more intriguing problem of the origin of these nucleons. Concerning that aspect of the origin problem, there are practically no experimental data (Fowler, 1964).

Equilibrium Theory

Several theories have been proposed as to the mode of formation of the chemical elements. One, which may be termed the equilibrium theory, proposes that the relative abundances of the elements are the result of a "frozen" thermodynamic equilibrium between atomic nuclei at some high temperature and density. By suitable assumptions as to the temperature, pressure, and density, good agreement with observed abundances is obtained for elements with atomic numbers up to 40 (Mason, 1967). For elements with higher atomic numbers, however, these assumptions lead to impossibly low abundances. On this account, theories have been proposed which consider the relative abundances of the elements as resulting from nonequilibrium processes. According to these theories the light nuclei were built up by thermonuclear processes and the remaining nuclei by successive neutron capture, with intervening beta disintegrations. This theory predicts the general trend of the observed data, but fails to explain some of the detailed features, particularly bridging the gap caused by the nonexistence of nuclei of atomic weights 5 and 8 (Mason, 1967). The difficulty can be overcome by postulating the fusion of three He^4 nuclei to give C^{12}.

However, the complexities of the abundance data as established by Suess and Urey (Mason, 1967), showed that no single process can satisfactorily account for these complexities. The problem was elucidated when they showed the feasibility of the following processes for the synthesis of the elements and their role in accounting for the observed abundances.

(1) Hydrogen "burning" to produce helium

(2) Helium "burning" to produce C^{12}, O^{16}, Ne^{20}, and Mg^{24}.

(3) Alpha particle processes, in which Mg^{24}, Si^{28}, S^{32}, Ar^{36}, and Ca^{40} are produced by successive additions of alpha particles to O^{16} and Ne^{20}.

(4) The equilibrium e- process, a statistical equilibrium between nuclei, protons, and neutrons, accounting for the abundance peak for iron.

(5) The s- process, in which neutrons are captured at a relatively slow rate, producing elements up to and including Bi^{209}.

(6) The r- process, in which neutrons are captured at a fast rate producing elements up to Cf^{254}.

Relative Abundance of Elements

Any theory of the origin of the elements should account for the formation of each elementary species which remained immutable and unchanged. It should also consider

the cosmic abundance of elements as its basis. The following sections will bring together the relationships between various factors which have direct relationship to the origin and abundance of elements.

The Composition of the Universe

The knowledge of the chemical composition of the universe is obtained mainly by spectroscopic examination of solar and stellar radiation. Also, analyses of meteorites and the composition of known planets such as earth are other aids in determining the composition of the universe. Spectroscopic observation indicates the elements responsible for the radiation. By a careful analysis of the intensities of the spectral lines, rough estimates can be made of the relative amounts of the different elements present in the outer layers of the radiating body. The data are consistent with the belief that the universe consists of the same elements throughout, except in minor local variations. Only once has an element not previously known to occur on the earth been discovered elsewhere; this was helium, first detected in the sun's spectrum.

Spectrographic evidence tells nothing about the composition of the interior of the planets. Therefore, it is necessary to employ analogies with the earth and the evidence provided by meteorites, which are parts of the solar system that eventually land on the earth.

Cosmic Abundance of the Elements

On the basis of data on the composition of meteorites and of solar and stellar matter, Goldschmidt (1954) compiled the first adequate table of cosmic abundances of elements and isotopes. The data on hydrogen and helium were discovered largely from an examination of the sun and stars, and the figures for most of the other elements were based on their relative abundances in meteoric material.

In general, the agreement between the relative abundances determined in different regions of the universe seems reasonably good (Mason, 1967). Variations in the abundances of hydrogen, helium, lithium, carbon, and nitrogen in different parts of the universe are due to the participation of these elements in thermonuclear transformations.

Figure 3 shows that the relative abundance of different elements, especially the lighter ones, varies considerably. An element may be a hundred or a thousand times more or less abundant than its immediate neighbor in the periodic table. Nevertheless, when the data are carefully analyzed, numerous regularities are found (Goldschmidt, 1954). These may be summed up as follows:

1. The abundances show a rapid exponential decrease for elements with the lower atomic numbers (to about atomic number 30), followed by an almost constant value for the heavier elements.

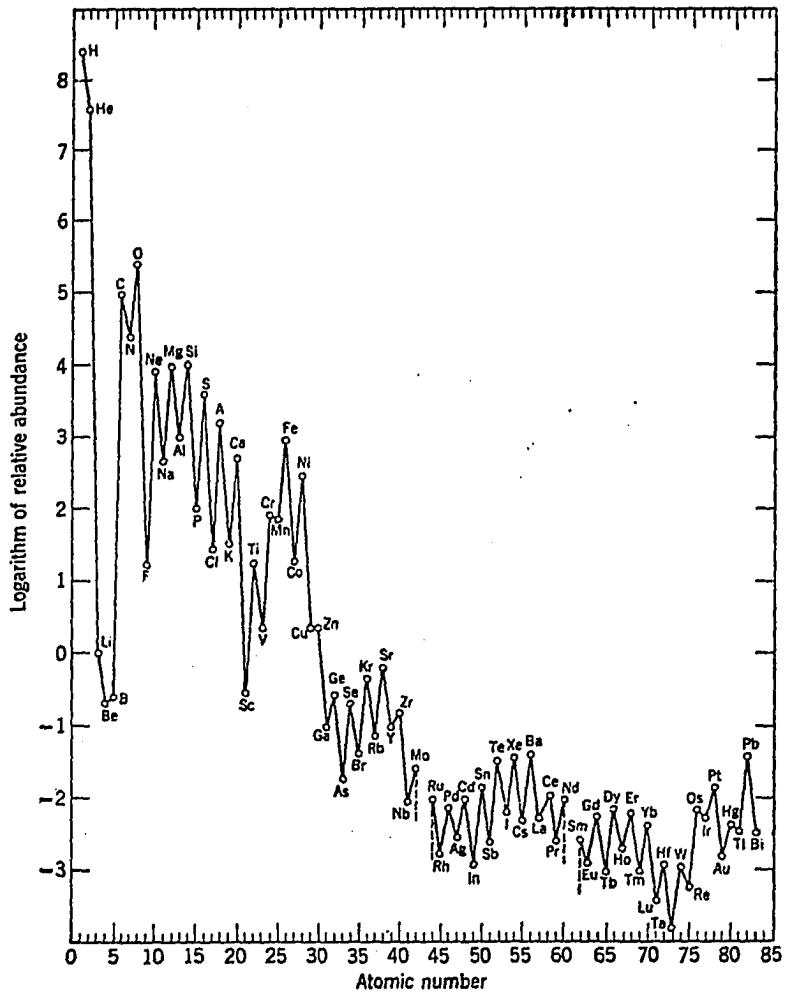


Figure 3. Relative abundances of the elements, referred to Si = 10,000 (atoms per 10,000 atoms of Si) plotted against atomic number Z (after Ahrens, 1965). Derived from terrestrial and solar data.

2. Elements with an even atomic number are more abundant than those with odd atomic numbers on either side. This regularity is known as the Oddo-Harkins rule.

3. The relative abundances for elements with higher atomic numbers than nickel (Z=28) vary less than those elements with lower atomic numbers.

4. Only ten elements--H, He, C, N, O, Ne, Mg, Si, S, and Fe--all with atomic numbers of less than 27, show appreciable abundance; of these hydrogen and helium far outweigh the other eight.

The regularities displayed in Figure 3 suggest that the absolute abundances of the elements depend on nuclear rather than chemical properties and are related to the inherent stability of the nuclei. An element is uniquely characterized by the number of protons (Z) in its nucleus, but the number of neutrons (N) associated with these protons can vary. As a result, an element may have several isotopes differing in mass number or atomic weight A(A=N+Z) and stability, but not appreciably in chemical properties.

Relatively few of the possible isotopes of any element are stable; of the total of 1441 isotopes (Evans, 1955) known to date, only about 280 are nonradioactive (stable); 66 are naturally radioactive, and 1095 are artificially radioactive. The implication is that an isotope is abundant because the combination of protons and neutrons in

its nucleus is a particularly stable one. On this basis the drop in relative abundances with increasing nuclear complexity can readily be explained; the absence from the earth of elements 43, 61, 85, and 87 is due to an almost complete instability of any nuclear arrangements for these atomic numbers. The total number of elements is 104, of which 81 are stable, 9 naturally radioactive, and 11 artificially radioactive.

Relative Abundance of Elements in the Earth's Crust

All available relative abundance measurements on terrestrial materials were compiled by Goldschmidt (1954). One clear-cut generalization from these data is that by weight, more than 85 per cent of the sampled earth consists of even -Z even -N nuclides. Only eight elements: O, Si, Al, Fe, Ca, Na, K, and Mg account for 98 per cent of the earth's total mass. The hydrogen in the oceans makes up only a small part of the remaining 2 per cent. The earth's crust consists almost entirely of oxygen compounds, especially silicates of aluminum, calcium, magnesium, sodium, potassium, and iron.

CHAPTER IV

ORIGIN OF HELIUM

Definition and Uses of Helium

The helium group gases consist of helium, neon, argon, krypton, xenon, and radon. They have been referred to as rare gases, noble gases, inert gases, helium group, group 0 (zero) or VIII elements. Helium is the lightest member of the rare gas family. It is an inert, monoatomic, colorless, odorless, tasteless inactive gas that is a good conductor of heat and electricity. It is the only substance that remains a gas below -423°F. It liquefies at -452°F and freezes only when placed under pressure and cooled to -458°F. When liquid helium is cooled to within 4°F of absolute zero, it assumes a physical state unlike any other known to science--a superfluid almost completely devoid of viscosity. In this state it is capable of flowing through the smallest openings and becomes a superconductor of heat and electricity.

The utility of helium is due to its unique physical properties: it diffuses more rapidly, flows through a hole faster, transmits sound at a higher velocity than any other

gas except hydrogen, conducts heat better, and it conducts electricity better than any other gas except neon (Cook, 1961). Compared to other gases helium has a much lower solubility in water than other liquids, a lower refractive index, and lower temperature of liquification. These properties are useful for many industrial and scientific applications, such as cryogenics, space flights, leak detection, arc welding, super conductivity, and medicine, to name a few.

Theories of Helium Origin

Due to a lack of stable compounds under natural conditions, the origin and occurrence of helium should be studied only with respect to substances which accompany it in nature. The most agreed upon theory on the origin of terrestrial helium is that this inert gas was produced by alpha emitters which are present in terrestrial materials. However, one should consider the possibility of partial entrapment of cosmogenic or primordial helium during the degassing stages of the earth.

Cosmogenic Helium

Cosmogenic or primordial helium is referred to as the oldest possible helium. This helium was first detected in the sun's spectrum by Lockyer in 1868 (Keesom, 1942). A look at the cosmic abundance of elements (Fig. 3) reveals

that helium is a major constituent of most stars. Hydrogen is the most abundant element in the universe and constitutes 76 per cent of its total mass (see Fig. 3). Helium, being the second most abundant element in the universe, makes up 23 per cent of the total mass of the universe.

Twelve to fifteen billion years ago the solar system was vastly different. At that time, according to current ideas (Fowler, 1964), it was a rotating mass of turbulent hydrogen gas. Conversion of gravitational potential energy into thermal kinetic energy caused the triggering of exothermic nuclear reactions. These reactions caused the fusion of hydrogen into cosmogenic helium and from there on into more complicated processes. The fusion or burning of hydrogen "fuel" into helium "ash" occurs in all stars, particularly in regions of the highest density and temperature. This can be written as

$$4H^{1} \longrightarrow He^{4} + 26.7 \text{ Mev}$$

Radiogenic Helium

It was not until 1895 that helium was definitely found on earth. This was done by boiling uraninite with sulfuric acid. Radiogenic helium is an end product of the decay of a parent element which is radioactive. Any artificially or naturally radioactive nuclide which is an alpha emitter is a good source of radiogenic helium. The following three reactions demonstrate the helium production from

a parent element.

$$U^{238} \longrightarrow Pb^{206} + 8\ He^{4},$$

Total half lives of 4.5×10^{9} years

$$U^{235} \longrightarrow Pb^{207} + 7\ He^{4},$$

Total half lives of 7.1×10^{8} years

$$Th^{232} \longrightarrow Pb^{208} + 6\ He^{4},$$

Total half lives of 1.4×10^{10} years

A brief look at Table (1) will reveal all the natural alpha emitters which, in turn, make up the summation of sources of radiogenic helium.

Since this study is primarily concerned with radiogenic helium, throughout this text the prefix "radiogenic" will be omitted. Therefore, in following discussions helium is meant to be radiogenic helium, and whenever cosmogenic or primordial helium is discussed, the proper prefix of "primordial" or "cosmogenic" will be used.

Theories of Association of Helium in Natural Gas

Rogers (1921), after giving a review of the occurrence of helium and considering the different possibilities as regards the origin of the helium contained in natural gas, concluded: (1) that the helium is derived from deposits of uranium or thorium, probably disseminated through the strata not far beneath the horizons at which the helium-bearing gas occurs, or (2) that the helium is derived from sources at great depth.

In favor of the first theory Rogers mentioned the following points: (1) The existence of such deposits is not unreasonable from the geologist's point of view. (2) If it is admitted that a considerable quantity of helium can escape from the mineral in which it forms and can migrate upward, the size of the parent deposit should be finite. (3) Such deposits would account for the areal and also the stratigraphic distribution of helium. Then he concluded that the theory of the radio-active deposits would account for this distribution of helium in natural gas.

Dobbin (1935) was of the opinion that the occurrence of many of the rich helium gases in reservoirs lying close to the crystalline basement rocks, which are relatively highly radioactive, is due to the radioactive elements present in the basement rocks.

Keesom (1942) suggested the idea that helium might have originated from the disintegration of the hypothetical element No. 87. To this, the idea of a generation of helium by short lived radioactive elements, which are totally extinct at the present time, may be added.

Pierce, et al (1964) pointed out in their discussion of helium in the natural gas that a few studies have been made since that of Rogers on the geologic occurrence of helium. They state that an increasing volume of data accumulated on the radioactivity of rocks has resulted in

a general acceptance or Rogers' assumption that most of the helium in natural gas is radiogenic.

Pierce, et al (1964) concluded that sedimentary rocks, and especially their asphaltic content, could be the source of the helium in the Texas Panhandle gas fields. Data on the distribution and composition of the natural gas suggests that three-fourths of the helium in the Panhandle field migrated into the field from the Palo Duro basin. It is believed, that the helium there, was derived from uraniferous rocks that are faulted against the gas producing reservoir rocks along the western boundary of the Panhandle field. The same authors also state that the relatively low concentration of helium in the natural gas migrated into the Panhandle field is from the Anadarko basin sediments. This helium probably was derived from traces of uranium and thorium in the same rocks which were the source of the hydrocarbon gas.

CHAPTER V

HELIUM GENERATING POTENTIAL OF ROCKS AND FLUIDS

Radioactivity plays a very important role in the geochemistry of helium. Unlike other rare gases, helium is formed as an end product of radioactive decay. It is being continually produced in the earth's crust by disintegration of uranium, thorium and other elements including polonium 210, radium 226, and samarium 150 which emit alpha particles. Since uranium and thorium are by far the most abundant radionuclides, other elements which are radioactive were not considered in this study. Furthermore, since the ratio of thorium to uranium is well documented in literature (25, 27, 33, 43), only uranium was considered here.

Helium generating potential, as defined in this study, is the potential or ability of certain elements or materials to generate helium. For example, the ability of uranium and thorium to generate helium is 1.16×10^{-7} ml (cc) of helium per gram of uranium per year, and for thorium is 2.43×10^{-8} ml (cc) of helium per gram of thorium per year (Rankama and Sahama, 1950). Consequently, the helium generating potential of any substance is its measure of

alpha emission activity. Since alpha activity is difficult to measure because of its absorption by exceedingly thin layers of material measured in a few microns in a solid, gamma activity is generally an acceptable substitute. Results of the gamma ray activity can be related to the alpha activity.

Method of Investigation

Most of the samples checked for Specific Radiation Activity (SRA) were chosen from the American Rock Collection (ARC) of Ward's Natural Science Establishment, Inc. This collection was assembled from the commoner rocks found on the North American continent, chosen from type localities in which very general classification schemes of rocks are satisfactory. Furthermore, each rock type in this collection, i.e., granite, is a sample which has average petrographic characteristics of all the granites.

Samples of the ARC and other rocks were crushed to obtain a homogenous particle size. Representative samples of the crushed rocks were weighted to an approximate 50.0 grams. This amount was desirable for the method employed to obtain specific radiation activity of each sample.

Equipments Used for Specific Radiation Activity Determination

The specific equipment used in this study is located in the Nuclear Engineering Laboratory of the University of

Oklahoma. The equipment consists of a 400-Channel Pulse Height Analyzer, Model 402 (By Technical Measurement Corporation) connected to an X-Y recorder, Model 2D2, all of which was connected to an IBM typewriter for the data print out.

Each sample was placed on a sodium iodide (NaI) thalium activated crystal mounted in a lead container (shield). As the gamma rays given off by the sample impinge on the crystal, a flash of light enters into a photomultiplier tube. This flash of light from the crystal strikes a photo-sensitive surface on the inside face of the multiplier tube causing it to emit electrons and change it to an electric signal. An important feature of scintillation counters is that each light pulse from crystal is proportional to the energy of gamma rays that produce the initial flash of light.

These signals are in turn counted and stored in 200 channels of the 400-Channel Pulse Height Analyzer. The other 200 channels are used to store forty minutes of background reading made prior to running the sample. After recording the gross counts from the sample for forty minutes and the background for forty minutes, the count was subtracted to obtain the net counts emitted by the sample (gross counts minus the background counts).

The results were plotted by the X-Y recorder with counts per channel vs channel number as shown in Figure 4.

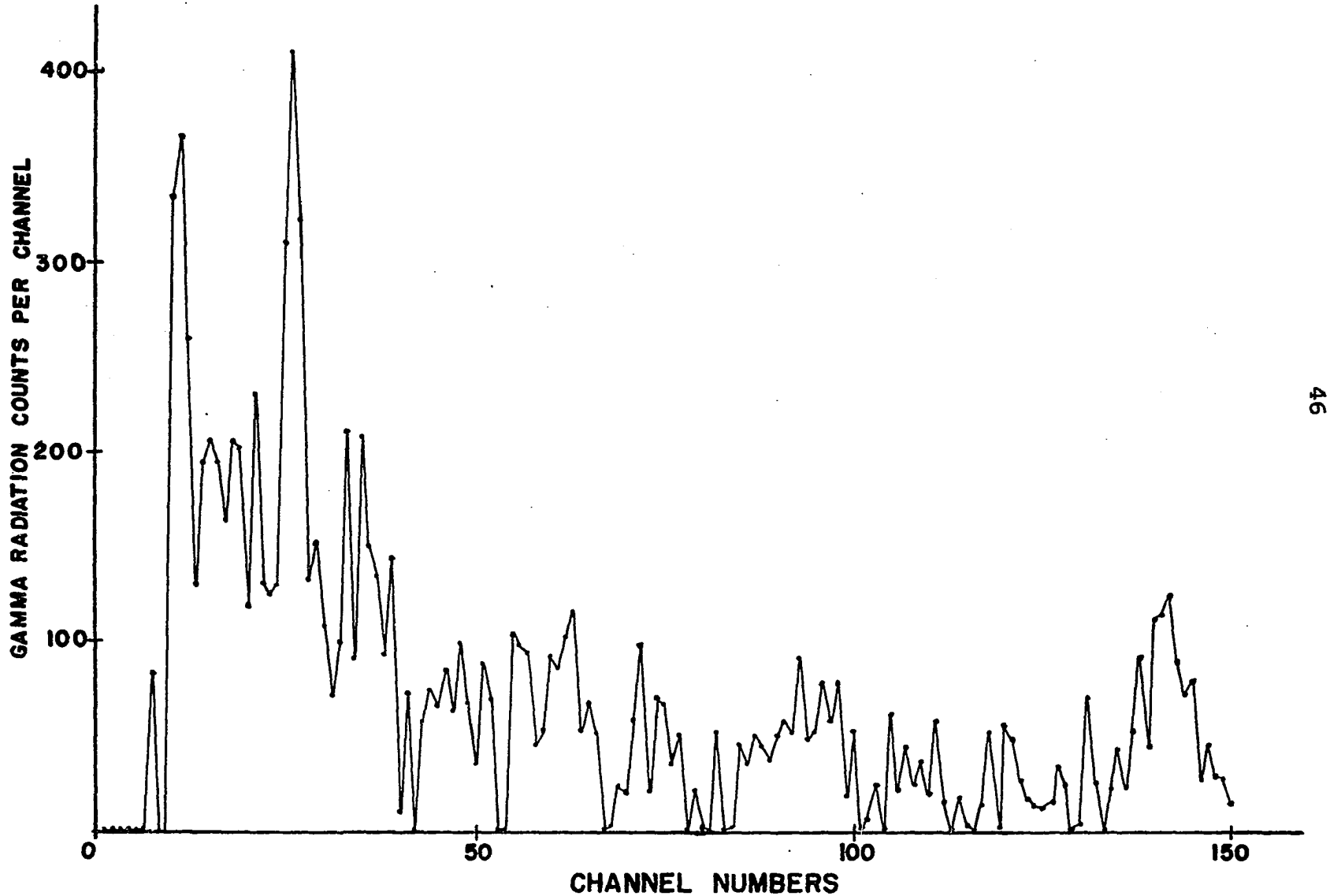


Figure 4. The net radiation diagram of alkali granite, ARC 13, from Norfolk County, Massachusetts (Mississippian). This diagram illustrates the total net gamma ray counts received in each of the channels.

Channels are numbered from left to right in sequence, as shown in Figure 5. The greater the channel number, the higher the energy (measured in Mev) of the gamma ray particles. This graph illustrates the total net gamma ray count emitted during the forty-minute time interval in each channel of the Pulse Height Analyzer and after subtracting the background, i.e., the net radiation from the sample. Typed results of net counts received in each channel of the Pulse Height Analyzer during the forty-minute time are numerically tabulated (Figure 5). The numbers listed in Figure 5 correspond to the counts per channel shown on the graph of Figure 4.

Theory of Specific Radiation Activity

The nature of gamma rays emitted were analyzed by "Gamma Ray Spectrometry" technique. The presence of uranium, thorium, potassium and their daughter products are detected by emission of gamma rays. Radiation counts recorded in the channels between 33 and 44 were used to determine the uranium content of the sample. The fundamental theory of the radioactive decay as expressed in Chapter II is expressed by dN, the number of atoms or radioactive matter which have disintegrated after a unit time. These in turn are proportional to the number of atoms, N, which have remained for the period, t, not being influenced by the disintegration process. Rewriting Equation (1a),

ARC Number 13, Alkali Granite, Norfolk County, Massachusetts (Mississippian) - Weight = 50.0 gm, 40 minute count.

00000	00000	99998	00000	99946	00001	00083	99970	99965	00335
00366	00259	00133	00194	00206	00194	00144	00206	00203	00119
00233	00130	00125	00129	00310	00411	00321	00134	00153	00108
00074	00100	00211	00090	00208	00151	00134	00093	00143	00010
00072	99951	00058	00074	00067	00084	00063	00099	00067	00036
00088	00070	99990	99995	00103	00097	00093	00045	00054	00091
00085	00102	00115	00052	00067	00051	99984	00002	00025	00020
00059	00099	00021	00071	00067	00035	00050	99989	00022	00004
99999	00053	99996	00002	00046	00036	00049	00043	00038	00051
00058	00052	00110	00048	00052	00079	00057	00079	00019	00053
00002	00006	00025	99990	00061	00022	00044	00024	00037	00020
00058	00015	99978	00019	00003	00001	00014	00052	00002	00056
00049	00027	00018	00017	00015	00017	00037	00025	00000	00004
00070	00025	99996	00030	00043	00023	00053	00095	00045	00112
00113	00124	00088	00073	00079	00027	00045	00029	00027	00015
00006	00000	99969	00004	00011	00028	99997	99991	00010	00016
00009	00006	00015	00015	00019	00004	00007	99992	00015	99999
99999	00007	99986	99998	00001	99986	99999	00010	00005	99990
00007	00017	00006	00014	00008	99998	99991	99996	00005	99999
00020	00010	99992	99994	00008	00003	00005	00002	00004	00006

	Left Cut	Right Cut	Spe. Rad. Act.
Peak on channel 33	74	90	0.0735
Peak on channel 35	90	93	0.1095
Peak on channel 39	93	72	0.1590
Peak on channel 44	58	67	0.0057
	Total Specific Radiation Activity		0.34770

Figure 5. Results of radiation counts recorded in each channel during the 40 minute time period after subtraction of the background radiation.

$$- dN = \lambda N dt$$

where λ is the proportionality constant or the decay constant or the decay constant.

The number of recorded counts is a measure of the number of atoms which have disintegrated. Therefore, dN is proportional to gamma ray counts or dN/dt is proportional to the number of counts/dt. Then, since $dN/dt = -\lambda N$, therefore, the counts/minute is proportional to λN. Next, if each side of the inequality of counts/minute is proportional to λN, is divided by the weight of the sample (grams), and λ is replaced by a new proportionality constant, L, then the equality becomes

$$\text{counts/gram - minute} = (L) \times (N/\text{gram})$$

where N is the number of atoms of uranium, which is proportional to the percent of uranium in a sample. Therefore, since N is proportional to grams of uranium, the above equation becomes

$$\text{counts/gram - minute} =$$
$$(M) \times (\text{grams of uranium/gram of sample})$$

where M is the new proportionality constant which includes the old one, L. But (grams of uranium)/(grams of sample) is the fraction of the sample which is uranium. Therefore,

knowing the per cent of the sample that is uranium and the corresponding counts/gram - minute for that respective sample, the proportionality constant 1/M may be calculated to use in transforming specific radiation activity (counts/gram - minute) into per cent uranium.

Two samples with a known value of U_3O_8 per cent were run on the Pulse Height Analyzer to determine their respective radiation activity.

Channels between 33 and 44 were chosen to determine specific radiation activity due to uranium. Calibration of a scintillation counter with known values or radiation activity due to uranium pointed out that in the region of the channels between 33 and 44 the least interference was involved. Most of the counts recorded between these two limits, therefore, are due to uranium only.

The calculation of 1/M, the proportionality constant, a sample of calculation of Specific Radiation Activity, and the known values of U_3O_8 are in the Appendix.

Helium Generating Potential of Igneous Rocks

The chief naturally occurring radioactive elements are uranium and thorium, both of which are widely distributed in rocks and in mineral deposits. The helium generating potential of igneous rocks or any other rock may be calculated if their uranium and thorium concentrations are known. As previously stated, only uranium will be considered

here. This is done because with the equipment used, the determination of thorium without great amounts of interference from other radioelements such as potassium was not possible. On the other hand, the general ratio of thorium to uranium of 3 to 1 is well established fact in the literature (1, 3, 15). Therefore, it is sufficient enough to calculate only the uranium content of the samples for determining its helium generating potential.

Nineteen igneous rocks representing every major rock type were examined for uranium content by gamma ray spectrometry. Fifteen of the nineteen igneous rocks were chosen from the American Rock Collection (ARC) and the other five from private sources. Table 3 illustrates the locality, age, name, measured Specific Radiation Activity (SRA), and uranium per cent of each sample.

Discussion of Results

Knowledge of the distribution of uranium and thorium in igneous rocks which make up most of the earth's crust is fundamental to an understanding of the helium generating potential of these rocks. The distribution of uranium and thorium is not yet well documented (Faul, 1954), because many problems of sampling, analysis, and interpretation remain. Although most of the fresh igneous rocks have a uranium content lower than 7 parts per million (ppm), some radioactive samples contain as much as 200 ppm uranium

TABLE 3

SPECIFIC RADIATION ACTIVITY AND URANIUM PER CENT
FOR IGNEOUS ROCKS

ARC No.	Locality/ County & State	Age	Lithology	Spec. Rad. Act.	Per Cent U
1	Lake Co, Ore.	Miocene	Obsidian	0.20175	5.9783×10^{-5}
2	Klamath Co, Ore.	Pleistocene	Scoria	0.17800	5.2759×10^{-5}
6	Chaffee Co, Colo.	Tertiary	Rhyolite porphyry	0.55050	1.6316×10^{-5}
11	Washington Co, Vt.	Devonian	Biotite granite	0.17650	5.2314×10^{-5}
12	Merrimack Co, N.H.	Late Paleozoic	Muscovite-Biotite granite	0.6850	2.0303×10^{-5}
13	Norfolk Co, Mass.	Mississippian	Alkali granite	0.34770	1.0305×10^{-5}
14	Essex Co, Mass.	Mississippian	Hornblende granite	0.29200	8.6548×10^{-5}
18	Teller Co, Colo.	Post-Oliogocene	Syenite	0.14725	4.3630×10^{-5}
26	Stoarns Co, Minn.	Precambrian	Granodiorite	0.48650	1.4419×10^{-5}
29	Siskiyou Co, Calif.	Late Tertiary	Hornblende andesite	0.13900	4.1199×10^{-5}
31	Essex Co, Mass.	Early Paleozoic	Diorite	0.34450	1.0210×10^{-5}
33	Chaffee Co, Colo.	Eocene	Vesicular basalt	0.17850	5.2907×10^{-5}
35	Somerset Co, N.J.	Triassic	Basalt	0.15200	4.5052×10^{-5}
37	Hampshire Co, Mass.	Triassic	Diabase	0.14225	4.2148×10^{-5}
41	Essex Co, Mass.	Early Paleozoic	Hornblende gabbro	0.23475	6.9565×10^{-5}
	Flagstaff, Ariz.	Recent	San Francisco peaks Lava Flow	0.71911	2.1314×10^{-5}
	Apache Co, Ariz.	Pliocene	Dineh bi Keyah oil field Syenite	0.32435	0.6122×10^{-5}
	Honolulu, Hawaii	Recent	Kilauea iki Lava Flow of 1960	0.27725	8.2162×10^{-5}
	LaPaz, Bolivia	Late Tertiary	Basalt from Andes Mnts.	0.17800	5.2759×10^{-5}

(Adams and Lowder, 1964). A high content of uranium and thorium usually can be correlated with other composition peculiarities. Some igneous rocks, especially those at or near the acid end of the series, are normally significantly more radioactive than other rock types.

The radioactivity of igneous rocks shows considerable variation. These variations are systematic, and are relatable to chemical, mineralogical, petrographic, and structural features of the rocks. Heinrich (1958) has demonstrated that the change in the uranium content of successive members of a magma series is less systematic than change in the major elements. This variability may stem from: (1) diverse paths open to trace elements during magmatic differentiation; (2) differences inherent in sampling techniques of igneous rocks; and (3) differences in post-crystallization histories of the rocks. Therefore, one can conclude that the uranium and thorium content of igneous rocks is a function not only of the initial concentration of these elements, but also the postcrystallization histories of rocks.

The difference between the values taken from literature (1, 27) and those obtained in this study seems to be due to calibration of the gamma ray spectrometer, interference from other radioactive sources such as radium and potassium, and the uranium used as a standard.

Nearly all igneous rocks contain trace amounts of uranium (Day, 1963). Much of the radioactivity in igneous rocks is concentrated in the mildly radioactive common accessories: zircon, sphene, and apatite. The highly radioactive minerals: monazite, allanite, uraninite and thorite, though much scarcer than common accessories, may be of widespread but spotty distribution in igneous rocks. These accessory minerals in granitic rocks are normally more erratically distributed throughout the rock than are the essential minerals. In general, rocks which are rich in magnesium, iron, and calcium, and poor in silica and alkalies, tend to be poor in radioactive elements; i.e., their helium generating potential is lower. Consequently, the helium generating potential of igneous rocks decreases from acidic to intermediate and basic types, respectively.

Unlike the major rock forming minerals, the amounts of thorium and uranium contained in the solid phases of the mineral assemblage forming at any particular stage depend not only upon concentration of those elements in the magma, but also upon the rate of precipitation of suitable host minerals, such as zircon, sphene and apatite (Mason, 1967).

A detailed petrographic analysis of igneous rocks of the ARC group yielded the following generalizations and conclusions. In igneous rocks radioactivity due to U and Th stems mainly from the following sources:

1. Moderately radioactive accessory minerals

2. Weakly to very weakly radioactive essential minerals

3. Interstitial material along grain boundaries and in structural defects of minerals

4. Fluid inclusions in minerals

5. Intergranular fluids

A maximum concentration of uranium and thorium is found in the youngest members of a series, regardless of the composition of the original magma. Most of the igneous rocks greatly enriched in uranium are late-stage differentiates of granite or syenite. These rocks approach pegmatitic composition, but not always the texture.

Geochemical Controls of U and Th Fractionation

During most of the magmatic cycle, both uranium and thorium, are in a tetravalent state, and the crystallization paths of both elements are parallel due to close similarity in ionic radii. During the intervals of crystallization when the water content of the melt is very low, magmas saturated with either constituent probably do not exist. Therefore, no precipitation of discrete uranium or thorium minerals takes place. Instead, their ionic radii and charge dictate that part of the U^{+4} and Th^{+4} which are present will enter appropriate host minerals. The U^{+4} and Th^{+4} affinity is probably for zirconium in zircon, and for calcium in apatite and sphene.

Uranium in unaltered igneous rocks occurs as U^{+4}. The uranium and thorium ions are concentrated in late magmatic fractions and in accessory minerals largely because their relatively large ionic radii hinder their entrance into the structure of the common essential silicates. Other factors governing the distribution of uranium and thorium are their low initial concentrations in magmas and their high valence.

Nearly all compounds of uranium and of thorium are known to be relatively insoluble in aqueous solutions in the laboratory (Faul, 1954). It seems possible that at some time during the "granite" stage, the buildup of water may so reduce the solubility of both uranium and thorium that sporadic precipitation of actual uranium and thorium minerals may occur. As differentiation proceeds to the highly hydrous pegmatite stage, more and more uranium forms discrete minerals and less and less enters common accessory minerals. Also, the low concentration of the two elements prevents the precipitation of phases in which they are principal constituents. They may also be concentrated in residual fluids to crystallize finally in the pegmatitic stages.

Helium Generating Potential of Sedimentary Rocks

Twenty-four samples of sedimentary rocks were checked for uranium content by gamma ray spectrometry. The samples

were chosen so different varieties representing various geologic ages of sedimentary rocks were analyzed. Of the 24 samples, 13 were selected from the American Rock Collection. The remaining 11 were from the Oklahoma Geological Survey and various other sources. Table 4 illustrates the results of the analyses of the sedimentary rocks.

Discussion of Results

The most widespread type of uranium deposits in the United States and that which will provide the bulk of uranium are the sedimentary rocks of the Colorado Plateau. Most of the uranium deposits in sedimentary rocks occur in clastic sediments of terrestrial origin. The bulk of uranium mineralization occurs as pore fillings and impregnations, with some replacement of organic material and replacement of the cement. Almost all the uranium contained in the earth is believed to be present in the upper lithosphere, preferentially concentrated in acidic igneous rocks, in part as discrete uranium minerals. Some uranium exists in the extremely thin intergranular films formed by solidification of the last residual traces of magmatic fluid (Heinrich, 1958).

Weathering of all types of rocks, releases uranium which may be deposited later in many kinds of sediments and rocks. Uraninite and pitchblende, which occur as primary constituents of some pematites, are readily altered during

TABLE 4

SPECIFIC RADIATION ACTIVITY AND URANIUM PER CENT
FOR SEDIMENTARY ROCKS

ARC No.	Locality/ County & State	Age	Lithology	Spec. Rad. Act.	Per Cent U
51	Livingston Co, N. Y.	Devonian	Calcareous Shale	0.15675	4.6445×10^{-5}
52	Monroe Co, N.Y.	Silurian	Argillaceous Shale	0.21125	6.2599×10^{-5}
53	Greene Co, N.Y.	Devonian	Arenaceous Shale	0.23350	6.9209×10^{-5}
54	Greene Co, Penn.	Pennsylvanian	Carbonaceous Shale	0.24438	7.2410×10^{-5}
58	Cuyahoga Co, Ohio	Mississippian	Gray Sandstone	0.18100	5.3648×10^{-5}
60	Middlesex Co, Conn.	Upper Triassic	Micaceous Sandstone	0.20925	6.2006×10^{-5}
61	Ulster Co, N.Y.	Devonian	Fine Grain Sandstone	0.16880	5.0032×10^{-5}
62	Hampshire Co, Mass.	Triassic	Feldspathic Sandstone	0.14600	4.3274×10^{-5}
63	Wyoming Co, N.Y.	Devonian	Argillaceous Sandstone	0.16625	4.9261×10^{-5}
69	Oneida Co, N.Y.	Ordovician	Argillaceous Limestone	0.05900	1.7487×10^{-6}
71	Erie Co, N.Y.	Devonian	Cherty Limestone	0.11800	3.4975×10^{-5}
74	Monroe Co, N.Y.	Silurian	Dolomitic Limestone	0.05775	1.7117×10^{-6}
75	Kent Co, Michigan	Mississippian	Gypsum	0.21400	6.3429×10^{-5}
	Canon City, Colo.	Cretaceous	Dakota Sandstone Uraniferous	8.65650	2.5658×10^{-5}
	Major Co, Okla.	Permian	Gypsum	0.06300	1.8673×10^{-6}
	Murray Co, Okla.	Ordovician	Dolomite	0.03600	1.0670×10^{-6}
	Murray Co, Okla.	Ordovician	Asphaltic Sandstone	0.33701	9.9886×10^{-5}
	Pontotoc Co, Okla.	Ordovician	Sylvan Shale	0.10975	3.2515×10^{-5}
	Carter Co, Okla.	Ordovician	Viola Limestone	0.18799	5.5723×10^{-5}
	Comanche Co, Okla.	Cambrian	Glauconitic Sandstone	0.19550	5.7946×10^{-5}
	Comanche Co, Okla.	Permian	Anhydrite	0.03750	1.1115×10^{-6}
	Comanche Co, Okla.	Permian	Halite	0.08000	2.3712×10^{-6}
	Comanche Co, Okla.	Ordovician	Simpson Sandstone	0.000	0.000
	Roger Co, Okla.	Pennsylvanian	Coal	0.33500	9.9294×10^{-5}

weathering processes to hydrated oxides, phosphates, and silicates; and some uranium is leached from them, probably as soluble uranyl complexes. Some uranium and thorium-bearing minerals, such as monazite, which is a primary constituent of igneous rocks, are not readily altered in place but are readily reduced by abrasion during transportation with clastic sediments. Some other minerals which carry uranium and thorium and which are minor primary constituents of igneous rocks are highly resistant to chemical decomposition and mechanical disintegration. These minerals, of which zircon is the most abundant, accumulate in placers and the heavy mineral fraction of clastic sediments. Most secondary uranium minerals are susceptible to alteration and leaching and are quickly reduced by abrasion during transportation with clastic sediments.

Uranium, which is dissolved in surface and ground water during alteration and weathering of rocks, may be redeposited nearby or may be carried into the drainage system and ultimately into the oceans. It is partially removed from aqueous solutions by precipitation as insoluble compounds, by adsorption on several kinds of sediments, and by substitution for calcium and possibly other elements deposited in chemical sediments.

The adsorption appears to be rather slight when deposition occurs in waters containing either free oxygen

or carbonate ion and increases markedly with decreasing oxygen and carbonate content. Inasmuch as uranium is readily dissolved by weathering processes and subsequently much of it is adsorbed by gel precipitates, clay minerals, and organic sediments, no highly concentrated deposits are formed by direct deposition of weathering products, and it becomes dispersed (generally) in sedimentary formations.

Types of Uranium Concentration in Sedimentary Rocks

Uranium is deposited epigenetically in all kinds of rocks and in many kinds of sediments by a variety of processes. It is introduced by hydrothermal solutions or ground waters and deposited where evaporation or the chemical environment causes precipitation. It is probable that some uranium is removed from aqueous solutions by adsorption in clays and other sediments.

Uranium existing in sediments and sedimentary rocks falls into three categories: (1) that which is indigenous (native) to clastic sediments; (2) that which is deposited syngenetically (formed contemporaneously) with sediments; and (3) that which is deposited epigenetically (later) after sedimentation ceases. It can be postulated that probably all clastic sediments contain some indigenous uranium. Syngenetic deposition of uranium occurs as many clays, evaporites, and carbonaceous sediments are laid down. Epigenetic deposition of uranium occurs in all types of

sediments and sedimentary rocks. Also, one should consider the fact that some sediments and sedimentary rocks contain uranium deposits resulting from two, or possibly all, of these categories.

Uranium which is indigenous to clastic sediments is contained partly in grains and fragments of discrete uranium minerals, partly in substituted form in other minerals, and possibly in part in intergranular films between the crystalline constituents of particles and pebbles of igneous rocks. Most of the indigenous uranium content of clastic sediments exists in heavy mineral, consisting of the chemically undecomposed residues of weathering i.e., sands, and gravel.

Syngenic deposition of uranium occurs predominantly in chemical sediments. Uranium may be removed from solutions by direct precipitation as insoluble compounds or by adsorption in several varieties of sediments. Uranium conpounds may be precipitated from solutions saturated by evaporation, and they may be precipitated from solutions which have become strongly reducing. The uranium or carnotite in coal is believed to be a result of the reducing environment produced by organic material in coal.

Helium Generating Potential of Metamorphic Rocks

The metamorphic rock samples for gamma ray spectrometry were crushed, like previous groups of rocks, in order to obtain a more homogeneous sample. Mathematically, a body

may be described as homogeneous if the value of some measured parameter varies randomly from place to place. The term random as defined here is the type of frequency distribution exhibited by randomly varying lithologic properties which are dependent on the nature of that property, i. e., Specific Radiation Activity (SRA).

The samples were selected from the American Rock Collection (ARC) so that common varieties of metamorphic rocks were represented. The helium generating potential for 7 of the metamorphic rocks in ARC have been determined. Table 5 illustrated such data as locality, age, name, Specific Radiation Activity (SRA), and the uranium per cent for the specific rocks analyzed.

Since there is practically no literature available on the distribution of uranium and thorium in metamorphic rock, it is not possible to compare and contrast the results obtained here with available data. However, the generalization made on the helium generating potential for the two previous rock groups is believed to be applicable for the metamorphic rocks.

Discussion of Results

The helium generating potential of metamorphic rocks is dependent on the uranium and thorium concentration of the parent rock which has been altered. Intense heat radiated from an intruding magma causes contact metamorphism. Regional metamorphism, which affects large areas, is the result of

TABLE 5

SPECIFIC RADIATION ACTIVITY AND URANIUM PER CENT
FOR METAMORPHIC ROCKS

ARC No.	Locality/ County & State	Age	Lithology	Spec. Rad. Act.	Per Cent U
79	Worcester Co, Mass.	Precambrian	Biotite Gneiss	0.11450	3.3937×10^{-5}
81	Clinton Co, N. Y.	Precambrian	Horneblende Gneiss	0.27050	8.0176×10^{-5}
83	Manhattan, N. Y.	Precambrian	Mica Schist	0.31150	9.2328×10^{-5}
86	Mitchell Co, N. C.	Precambrian	Hornblende Schist	0.02200	6.5208×10^{-6}
91	Washington Co, N. Y.	Cambrian	Red Slate	0.09850	2.9195×10^{-6}
93	Sauk Co, Wisconsin	Precambrian	Quartzite	0.11950	3.5419×10^{-5}
96	Pickens Co, Georgia	Cambrian	Pink Marble	0.0925	2.7417×10^{-6}

both pressure and heat upon deeply buried rocks. In both types of metamorphism, fluids in the rock will aid the chemical changes. Water is the principal fluid, but in addition such chemical elements as chlorine, fluorine, boron, and others may emanate from intrusive masses and react with the surrounding rocks. Many minerals are stable only within limited ranges of pressure, temperature, and chemical condition. Upon metamorphism, changes such as recrystallization and chemical recombination (generally oxidation in case of uranium) will occur.

Helium Generating Potential of the Fluids

Commonly, as much as 40 per cent of the uranium in most fresh-appearing igneous rocks is readily leachable (Faul, 1954). The exact distribution of this radioactivity is largely unknown. Leachable radioactivity may occur: (1) in altered structure of primary silicates; (2) as interstitial materials derived from late magmatic or hydrothermal solutions; (3) in partly soluble radioactive accessories; and (4) as adsorbed ions in disseminated weathering products such as iron oxide, and also at grain boundaries. The distribution of uranium, however, may be modified by the leaching action of surface and ground waters, resulting in some cases in a diminished uranium content. This uranium diminition is pointed out by Heinrich (1958) who believed that in particular cases diminished phosphate

content is accompanying somewhat increased uranium content. Moreover, it is believed that connate water and petroleum could partially leach out the uranium and thorium in sedimentary rocks. This leaching is believed to have taken place subsequently to migration of oil and brine solutions into traps. After entrapment of these fluids, they are alpha emitters and hence have the potential to generate helium.

The existence of uranium and thorium in percolating ground waters and thermal springs is well documented (Adams and Lower, 1965). The petrographic study of some uranium bearing ores makes this generalization possible: the inverse relation between grain size of the apatite nodules and their uranium content is constant for a certain mining district. This relation precludes downward percolation of ground waters as a source of uranium, because this relation holds in finer grain deposits. Therefore, any downward movement of uranium-bearing solutions through this kind of deposit would enrich the finer grain nodules.

Procedure

To determine whether the fluids such as brines, crude petroleum, and ground water have the ability of transporting uranium and generating helium, representative samples of such fluids were examined by gamma ray spectrometry. The experimental apparatus used here is in School of Petroleum

and Geological Engineering, the Reservoir Mechanics Laboratory of the University of Oklahoma. Figure 6 is a schematic drawing of this equipment. It consists of a core holder, a reservoir tank, and a monometer. The core holder was a hollow cylindrical lucite tube. A hypothetical unconsolidated rock consisting of a homogeneous mixture of Simpson and (Ordovician) and 50.0 grams of radioactive material per each core filling was used. The radioactive material was highly uraniferous Dakota sandstone (Cretaceous) from Oklahoma Geology Camp Area, Canon City, Colorado. Simpson sand was chosen because it is essentially free of radioactivity.

Great care was taken in mixing the Simpson sand and radioactive material to insure a homogeneous mixture of the two, which was used for the core fillings. Different types of fluids were injected into the cores were intended to dissolve, carry away or leach out part of the uranium mineral from the unconsolidated sandstone packed in the cylindrical core.

Various kinds of fluids such as tap water and crude oils of different API gravity were injected into the separate cores for each run. The injected fluids were tested for radioactive content before injection to the core and after they had flowed through the core. These analyses were carried out to determine the following:

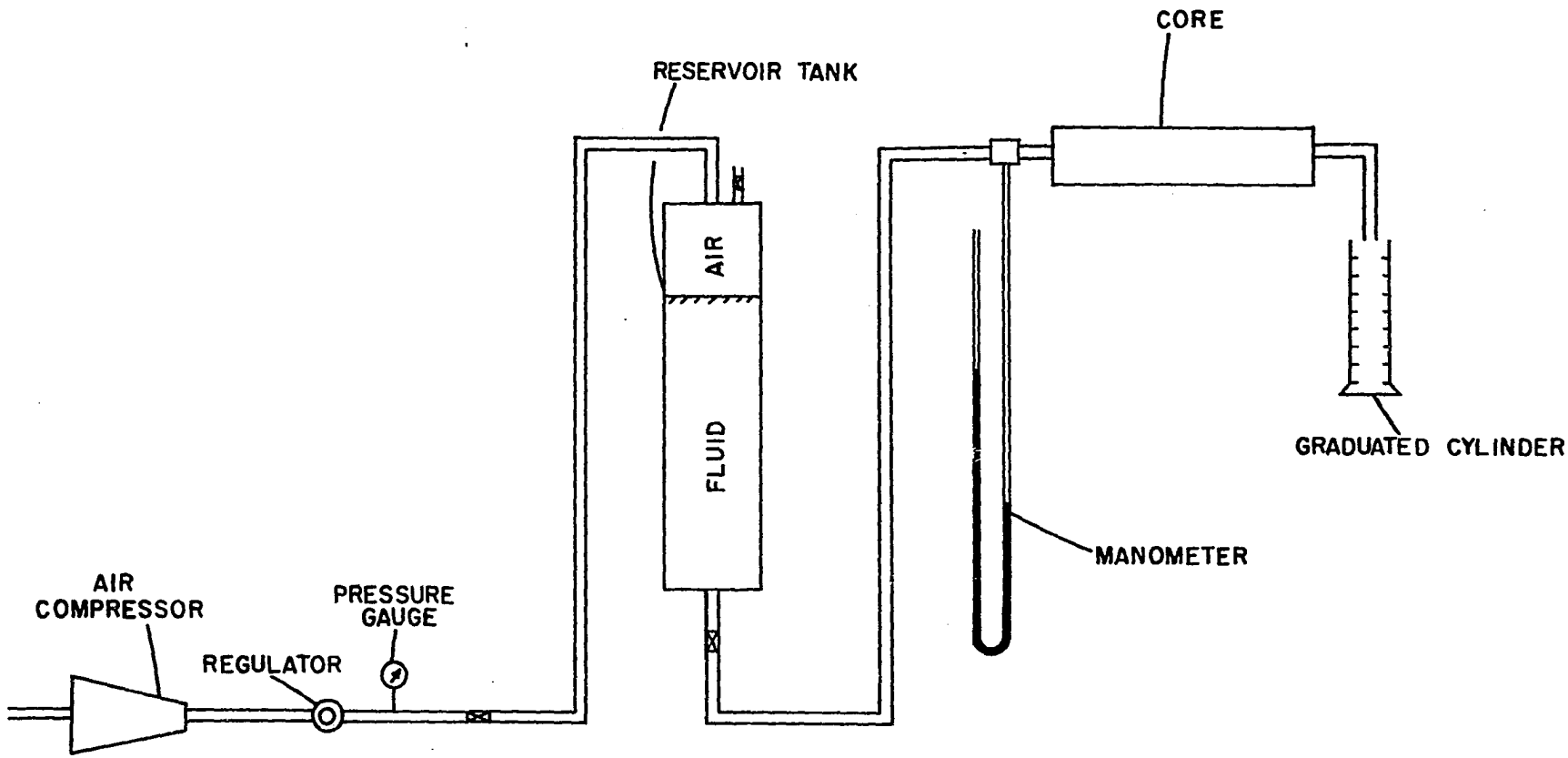


Figure 6. Schematic drawing of the apparatus used in leaching uranium out of an unconsolidated sand mixed radioactive material.

(1) The helium generating potential of fluids such as ground water, crude oil, and brines. This part illucidates the fact that the thorium and uranium within host rocks could have partially lost their alpha emitters while these fluids are migrating toward the traps. After dissolving or leaching some of the uranium and thorium, fluids such as brines (connate water) and liquid petroleum become alpha emitters. Therefore, they have the ability to generate helium while they are in the trap.

(2) Determination of the amount of leached out radioactive material by the various kinds of fluids used here. This fluid which was collected at the outlet of the core is termed radioactive filtrate.

(3) Determination of the Specific Radiation Activity of the sand (hypothetical rock in this study) used in core fillings after the passage of different kinds of fluids. This is termed the sand residue.

The pressure drop across the core was just sufficient enough to establish the flow. After collecting 1000 ml of injected fluid at the outlet of the core, 200 ml were analyzed for the uranium content dissolved in it. The results of this experiment are tabulated in Table 6.

Considering the results tabulated and stated in the previous sections of this chapter, one can conclude that all the three categories of rocks have the ability to

TABLE 6

SPECIFIC RADIATION ACTIVITY AND URANIUM PER CENT FOR FLUID AND CORE FILLINGS

Description	Spec. Rad. Act.	Per Cent U
Tap Water, University of Oklahoma, from Garber Sand (Permian)	0.11570	3.24293×10^{-5}
24.7 API° Crude Oil, from West Texas	0.000	0.000
37.5 API° Crude Oil, from West Texas	0.00353	1.0463×10^{-7}
Radioactive filtrate, tap water after passing through the core	0.181250	5.370×10^{-5}
Radioactive filtrate, 24.7 API° Crude oil after passing through the core	1.95818	5.803×10^{-4}
Radioactive filtrate, 37.5 API° Crude oil after passing through the core	0.37970	1.1254×10^{-5}
Radioactive sand residue-after flow of tap water	35.9676	1.066×10^{-3}
Radioactive sand residue-after flow of 24.7 API° Crude oil	34.33749	1.017×10^{-3}
Radioactive sand residue-after flow of 37.5 API° Crude oil	36.44626	1.0802×10^{-3}

generate helium. Needless to say, the magnitude of the generating potential of every rock or mineral specimen is a direct function of its alpha emitters. Uranium concentrations much higher and lower than the ones presented in Tables 3, 4, 5, and 6 do exist. These concentrations may be considered exceptional and local.

Comparison of the above tables points out that igneous rocks are generally richer in uranium deposits. Nevertheless, one should remember that almost all of the uranium mined in the United States is within sedimentary rocks. Morrison formation (Jurassic) of Colorado is the major uranium bearing formation in the United States. Also the fluvial sediments of the same age in Colorado and Utah are major sources of uranium. These formations are generally bedded sandstone deposits with complex of uranium. Consequently, one can postulate that sediments and sedimentary rocks are potential helium producers. Also, the movement of fluids such as brines and crude oil through porous media enriched in uranium and thorium could yield fluids rich in alpha emitting elements.

Some crude oils are appreciably radioactive (Heinrich, 1958) and abnormal concentrations of radioactive elements and their decay products including U and Th have been found in some oil fields of the United States. Although only one of the crude oils used in this study showed traces of radioactivity, this study indicated that crude oil has

the ability to leach uranium compounds from the host rock. The uranium and thorium in petroleum may be present as colloidal particles or as dissolved metallo-organic complexes. If they are present in colloidal form, the uranium content of the source rock would have to be relatively large. If they occur in solution, it is expected that they are concentrated in a surface-active fraction coating the pore walls of the reservoir rock. The latter theory is more likely to be true, because the large concentration of uranium and thorium in the reservoir rocks is improbable.

Heinrich (1958) estimated that the average uranium content in petroleum is 100 gm/ton. The highly variable radioactivity of petroleum and the fact that crude oils from nonuraniferous provinces contain only negligible amounts of uranium (Pierce, 1955) suggest that uranium in petroleum is epigenetic (later origin than the petroleum itself). Also, a study of compositional analyses of many natural gases from uraniferous provinces, i. e., Colorado Plateau, New Mexico, and Arizona confirms the fact that high helium content of these gases is due to high uranium concentration of the reservoir rock. The highest helium concentrations in the natural gases coincide with the presence of uraniferous asphaltites. This fact is concluded from relatively high Specific Radiation Activity of the asphaltic sandstone (Ordovician-Oklahoma) in Table 4. The association of gamma

ray anomalies, uraniferous asphaltites, radium bearing brines (Scott, 1968), and uranium bearing petroleum, suggests that the major part of the helium is radiogenic, derived from petroleum source rocks and rocks through which they have moved. Further support of this theory lies in the fact that generally the helium content of natural gases increases with the age of the reservoir.

The association of uranium with asphaltic materials could be explained in three general ways:

1. The uranium was transported in petroleum, which was subsequently oxidized; the uranium may have been reconcentrated subsequently. But the organic material and the uranium are essentially contemporaneous.

2. The asphaltite represents material derived from petroleum present in the rocks prior to uranium mineralization and subsequently served as a precipitant for uranium. A variation of this idea states that hydrothermal solutions depositing uranium also converted petroleum to asphaltite (Smith, 1963).

3. The uranium was deposited first as uraninite (UO_2) and subsequently served to polymerize (change into same compound with higher molecular weight and different physical properties) petroleum or natural gas to liquid phases that partly dissolve and replace pre-existing uraninite.

CHAPTER VI

DISTRIBUTION AND OCCURENCE OF HELIUM

Knowledge of the distribution of uranium and thorium in specific regions of the outer crust is fundamental to the understanding of the potential helium generators and the earth's heat flow. The abundance of the radioactive elements and the heat flow data may have a close correlation with helium generating potential of these rocks in any specific region. The rate of production of helium is 1.16×10^{-7} cc/gm of uranium per year, and 2.43×10^{-8} cc/gm of thorium per year. Uranium concentration in granites, which are the major constituent of the earth's crust is estimated by various authors (1, 15, 25) to be 3.2×10^{-4} to 6.4×10^{-4} per cent. Rankama and Sahama (1950) give the helium content of igneous rocks as 0.003 gm/ton, and state that helium content in these rocks are never more than 10^{-4} cc per gram.

Occurrence

Extraterrestrial

Stellar spectroscopy has revealed the regular existence of helium in the hotter stars. Helium is present in

the sun's atmosphere, whereas other inert gases are absent. The high cosmic abundance of helium (23% of the total mass of the universe) is explained by the energy-producing thermonuclear processes which take place in the interiors of the stars (Mason, 1967). This process, as mentioned in Chapter IV constantly changes hydrogen to cosmogenic or extraterrestrial helium.

Terrestrial Helium

Helium and its natural isotope, helium^3 are present in minerals, rocks, natural gases, sea waters, thermal springs, and in the atmosphere in highly variable proportions. It has been suggested (Keesom, 1942) that some of the helium^4 is primordial. Primordial helium is the oldest helium (cosmogenic) which was one of the major constituents of the original gaseous phase, at the beginning of the earth's history. This would indicate that some of this helium gas has accumulated in suitable traps in the earth's crust as a result of the degassing of the earth. However, there is general agreement that most of the helium gas in the crust is a product of alpha decay.

The helium content of common rock is very low, compared to minerals such as beryl, and spodumene. A metric ton of granite containing 2 ppm of uranium and 10 ppm of thorium will produce 0.22 + 0.29 ml or a total of 0.51 ml of helium at standard temperature and pressure per million

years. Most of that helium will be trapped in the crystals of the rock, but some of it may be released by recrystallization and migrate into whatever porous formation or passageways are available. Also, some of the helium could flow through fractures which appeared after the consolidation of the host rock.

One general problem concerning helium is its scarcity in terrestrial material. There is good reason to believe that the present day atmosphere of the earth is of secondary origin (Mayne, 1956). In the process of planet accretion the volatile components, including the rare gases, are likely to have been largely lost from the primitive earth. The present atmosphere was developed chiefly by a process of degassing and weathering throughout the life of earth. There seems to be little doubt that practically all of primordial helium was lost (Mason, 1967), and that present-day terrestrial helium is the result of nuclear disintegrations during the lifetime of the earth.

Crustal Erosion

Rock weathering will release the gases occluded in the crust to the atmosphere. An early estimate of the amount of weathered rock, based on the sodium content of the oceans (Clarke, 1924), gave a value of 8.33×10^{23} gram, and this was substantiated by Goldschmidt in 1954. Mayne (1956) has calculated the minimum amount of helium thus released in

10^9 years to be about 2×10^{17} gram or 1.5×10^5 atoms of helium/cm^2-sec for the whole earth's surface. This cannot be the main source of supply of the helium to the atmosphere. However there is reason to believe that rocks may lose a fraction of their gas by erosion, at least if it is radiogenic. Nevertheless one should consider that all the rare gases in the atmosphere are mostly due to continuous degassing of the earth, not due to crustal erosion. In fact, there may be additional loss of gas due to leakage even after the cooling of the earth.

Helium in Crustal Rocks

The rate at which helium is generated in the crust is determined by U an Th content of the crustal rocks. Fleischer (1962) summarized all of the available data on the radium content of granitic and basaltic rocks, and from this information it has been deduced (assuming Th to U ration of 3.5) that helium production in these rocks is approximately 3.5×10^{-3} ml/gram and 0.5×10^{-3} ml/gram in 10^9 years respectively for each rock type. The granitic mass of the crust is 15×10^{24} grams and the mass of basalt to a depth of 5 km underlying the continents is 7.5×10^{24} gram as estimated by Mayne (1956). Table 3 and other sources (1, 2, 15, 33) confirm higher uranium content for granitic rocks than the basaltic rocks. Therefore one may conclude that the over-all helium generation in the crust is coming from the surface granitic layer.

The following abundance values given by Rankama and Sahama (1950) are considered most reliable. For thorium, the average concentration for igneous rocks in general is 11.5 gram/ton. Other thorium concentrations in igneous rocks are: (1) for acidic rocks 13.0 gm/ton, (2) for intermediate rocks 9.97 gm/ton, and (3) for basic igneous rock 5.0 gram/ton. The uranium concentrations in terms of gram per ton are 3.96, 2.61, 0.96 for acidic, intermediate, and basic igneous rocks, respectively. Thorium to uranium ratio of igneous rocks is 3.2, 4.0, 4.5 for acidic intermediate and basic rocks. These values elucidate on the potential of helium generating rocks and also on the probable amount and distribution of helium in these rocks. Finally the sedimentary rocks have the potential to generate helium according to their local concentration within the sedimentary section. Goldschmidt (1954) gave the following U and Th concentrations for the sediments: arenaceous sediments (sandy), 5.4; argillaceous (clayey) 12; shales 10; and limestones 1.1, all in units of gram per ton, thorium concentration. The uranium content of sedimentary rocks is 1.1 gm/ton as an average value for all the marine sediments.

Helium has a geological occurrence and distribution that is unique among the elements. On the average, it is continuously increasing in amount in the earth's crust, being formed at the expense of the elements that are alpha emitters. On the other hand, the crust is continuously losing

helium at a rate that is less than the amount being formed by the alpha emitters. Mayne (1956) has concluded that helium is generally increasing in the earth's crust. Therefore the amount of helium in the crustal rocks is related to the age of these rocks and their content of uranium and thorium.

Almost all commercially significant deposits of helium are in the southwestern United States, in Kansas, Oklahoma, the Texas panhandle, and New Mexico. These natural gases containing helium are present in carbonate rocks of Permian Age. Therefore, there are only a few gas pockets in the earth's crust that contain helium. The helium content of natural gases may range up to about 10 per cent. Natural gases from different fields and even different geological strata in the same field may differ widely in chemical composition and helium content. It has commonly been assumed that helium ratios are low in host rocks, because helium atoms diffuse through the crystalline lattice structure. However, one can give the possible cause(s) of the helium variation in natural gas as one, or combination of, the following factors:

(1) The uranium and thorium concentrations in the host rock which generates the helium.

(2) The geologic age of the source rock. It could be safely generalized that the U and Th are more abundant in

the relatively younger rocks. As the age of the rock increases the helium content or the helium generated from that particular rock increases too. On the other hand the uranium and thorium concentrations will decrease with increasing age.

(3) Selective leakage and retention of helium which is a function of mineral content, bulk density, crystal structure, grain size, cleavage, and fracture. These passageways may transport the original helium in situ to suitable traps and therefore cause a variable helium ratio.

(4) Conditions such as localized high concentration of alpha emitters in sedimentary as well as basement rocks could be a good reason for high helium content of some natural gases. Also, the heating of a body of rock can cause a rapid helium migration to cooler environment. The source of heating is magmatic intrusions, and regional or contact metamorphism.

Helium in the Hydrosphere

The general presence of helium in oceans and mineral springs in minute quantities indicates very slight solubility of this inert gas in waters. This fact has been studied by several authors (Bieri, 1967 and 1968) who have analyzed the sea waters extensively. It is believed that this helium in waters of different oceans comes from an influx of this gas through the bottom of the ocean. Therefore, upon examining

all the available data, one could postulate that the helium is attributed to the decay of U, Th and their daughter isotopes in the basaltic layer of the earth's crust underlying all the oceans. The degassing of the earth may have also contributed to the amount of helium present in ocean waters. The solubility of helium in sea water increases with depth, and it decreases with a decrease in temperature, and an increased salinity.

Helium in Atmosphere

The abundance of helium in the atmosphere is proportional to its rate of release from the crust and the rate of its escape from the earth's gravitational field. Many authors (8, 17, 20, 26) have assumed that the atmosphere is now in equilibrium with respect to helium abundance. Therefore the escape rate must be equal to the rate of crustal liberation. The helium formed in the crust, gradually works its way up into the atmosphere.

On the basis of spectroscopic evidence, an abundance figure for helium in the universe has been estimated as 3.5×10^{7} atoms per 10,000 atoms of silicon (Fig. 3). The comparable figure for the abundance of helium in earth is only 3.5×10^{-7} (Tiratsoo, 1967), so there is a considerable deficiency factor involved here. It is assumed that due to its lightness there has been a steady loss of helium from the earth's surface to the atmosphere and then to space.

This loss to space therefore is due to escape of this small atom from the gravitational field of the earth which is not strong enough to retain helium. The current concentration of helium in the atmosphere is 4 ppm (0.0004 per cent), although more recent literature (Badwahr and et al, 1969) suggest value of 5.2 ppm for helium content of the atmosphere.

CHAPTER VII

MIGRATION OF HELIUM

Introduction

Helium would have been much more plentiful in crustal rocks and the atmosphere if it were not due to the fact that helium atoms are so light and small that they continue to escape from the host rocks. Several factors influence the rate of escaping, such as the physical characters of the environment, temperature, and pressure. As an example of migration of helium one could postulate localities where helium rich natural gas exists without a source rock which is rich in uranium, thorium, and other alpha emitters. The high helium content may be explained by the fact that at once stage of the heating helium had escaped to cooler environments and was trapped by overlying impermeable barriers. Furthermore, the distribution of this rare gas in all parts of the universe is a clear evidence of its migratory nature, and its capability of moving from the sites of its generation.

Migration of Alpha Emitters

As seen in the measurements made on the leaching of uranium and thorium from rocks (Chapter V and Table VI), water, and crude oil have the ability to transfer the alpha emitters in situ and carry them away. Therefore it is clear to acknowledge that fluids such as brines and ground water have also this ability. The presence of minor gamma ray activity in tap water analyzed in this study and waters of different origin analyzed by other authors (1, 12, 59, and 67) confirms the fact that radioactive materials are leachable and could be partially carried away from the original site. The modes of migration suspected here are either: (1) radioactive materials are slightly in solution because of their solubility factor, and (2) they are in colloidal or suspension form and move along with the carrier.

Migration of Helium at High Pressures

Amyx, Bass and Whiting (1960) showed in an extension of Klinkenberg's original work (1941), that porous media exhibit relatively high apparent permeabilities when subjected to low pressure gas flow. This deviation, however, as defined by Klinkenberg's relationship is:

$$K_a = K \left(1 + \frac{b}{p_m}\right)$$

where: K_a = apparent permeability

K = true permeability

b = constant

p_m = Mean pressure = $1/2\ (p_1 + p_2)$

occurred only in the range of below 100 psig. Above 100 psig all gases studied by Klinkenberg and Amyx, Bass and Whiting flowed similarly through the permeable media. At this pressure of 100 psig, each media yielded an essentially similar value for the absolute permeability. Figure 7 shows a plot of the apparent permeabilities vs. mean flowing pressure in cm of mercury for various gases.

It can be postulated that helium in pure state will never occur or has been occurred at pressures of 100 psig magnitude, because its generation is an extremely slow process. After production, this gas usually will migrate away from the side of its generation. Consequently, it cannot be entrapped in place at a rate which permits a gradual pressure buildup of 100 psig in magnitude. Moreover, if such an impossibility occurs, i. e., helium has accumulated to pressures around 100 psig magnitude, it flows almost like any other gas, as indicated in Figure 7.

Migration of Helium at Low Pressures

Migration of helium at low pressures, i. e., below 1 psig, may occur only if the generation rates of helium are

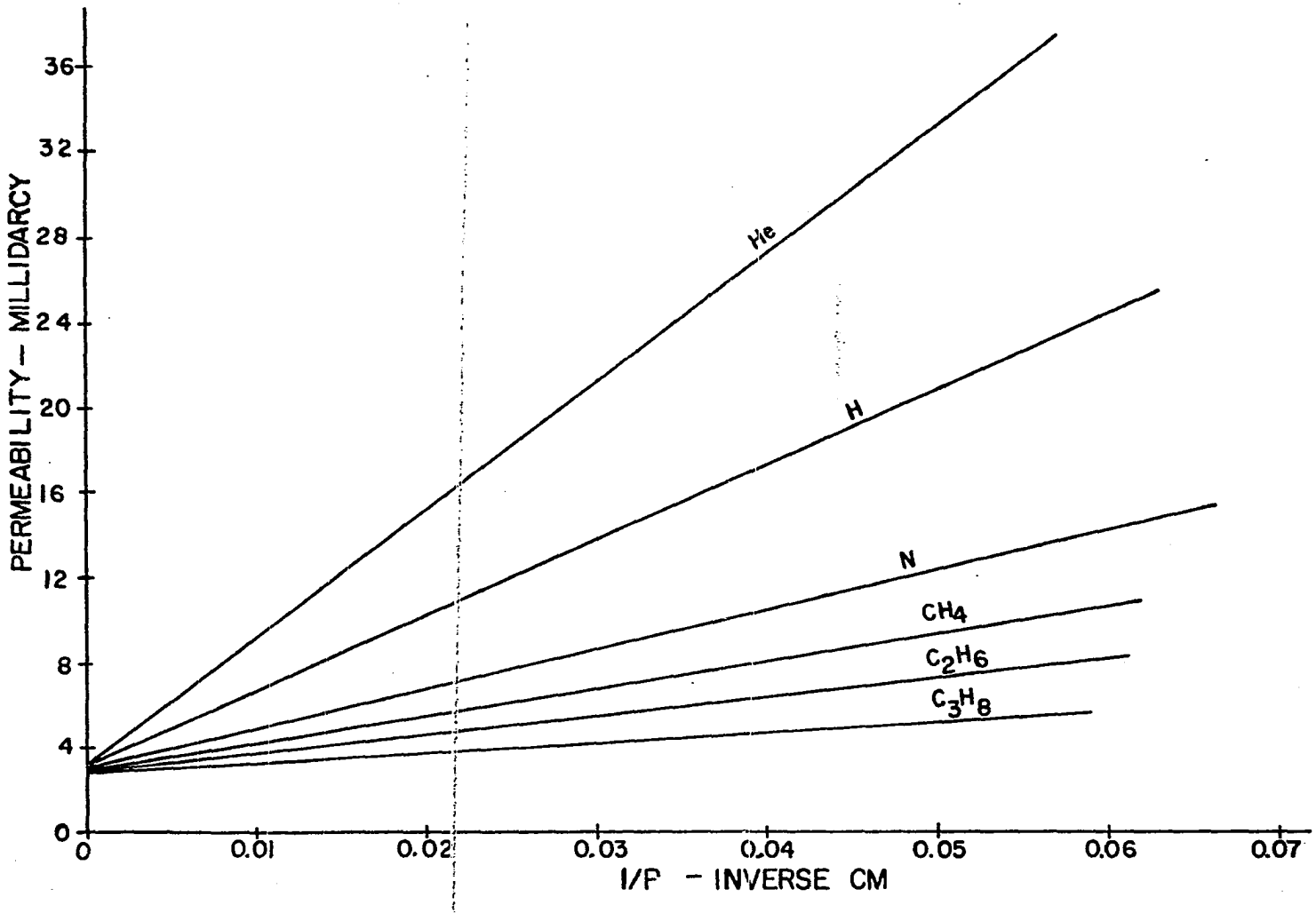


Figure 7. Gas apparent permeabilities vs inverse of the mean pressure.

exceedingly high and sufficient pore space is available. The pore space may be some distance from the generation site, or somewhere close to it, that is, this hollow space may be in the form of a cavity or the actual pore space of the rocks in situ to trap and hold the helium. This situation could occur in nature, especially in sedimentary rocks, where local concentration of uranium and thorium is unusually high, and associated porosities are high also. The helium thus generated could accumulate in pore spaces and probably in leached out limestone caverns. With a slight buildup of pressure, which is in a sense the accumulation of helium at a rate which exceeds its escape, the entrapped helium could migrate when the required pressure is reached by its accumulation to establish the flow.

To study the characteristics of this movement at a low pressure of 0.262 atmospheres (200 mm of mercurey), 71 core plugs were used. Most of these core plug samples had dimensions of 3.90 cm in length, and a diameter of 2.52 cm. These 71 core samples were taken mainly from those available at the Core Library, of the University of Oklahoma, with a few from other sources. Care was taken to obtain a broad spectrum of rock types from the avialable core. Also, the exact depth and lithology of the samples were checked for accuracy against electrical log diagrams. Of the 71 cores, 62 were selected from the Morrow formation (Pennsylvanian)

and Chester Limestone (Mississippian), from the original whole cores available at the Core Library. The remaining 9 were igneous rocks: 2 from a well in Apache County, Arizona, and 7 from outcrops at different locations. The cores obtained from oil or gas wells have a prefix of H or V, denoting that the core was cut horizontal or vertical, respectively, to the bedding plane. The 7 cores obtained from outcrops do not have any type of prefix. The numbers following the "H" or "V" are the depth in feet at which the core was cut.

The 71 samples were analyzed to determine their transmitting ability of helium at a relatively low pressure of 0.262 atmospheres (200 mm of mercury). Morrow formation cores were used extensively, because it consists of sandstone, limestones, and shales of various composition and physical characters. The helium and air flow rates at a pressure differential of 0.262 atmospheres for each core were measured by a Soap Bubble Meter and a stop watch at room temperature (80°F). Figure 8 is a schematic drawing of the apparatus used for flow rate measurements. Porosities were determined by a Digital Volt Meter porosimeter at the Core Laboratories in Oklahoma City, Oklahoma. Table 7, is an arrangement of the data obtained by analyzing the core plugs. It gives the drilled depth, location, lithology, air and helium flow rates in units of cc per second under

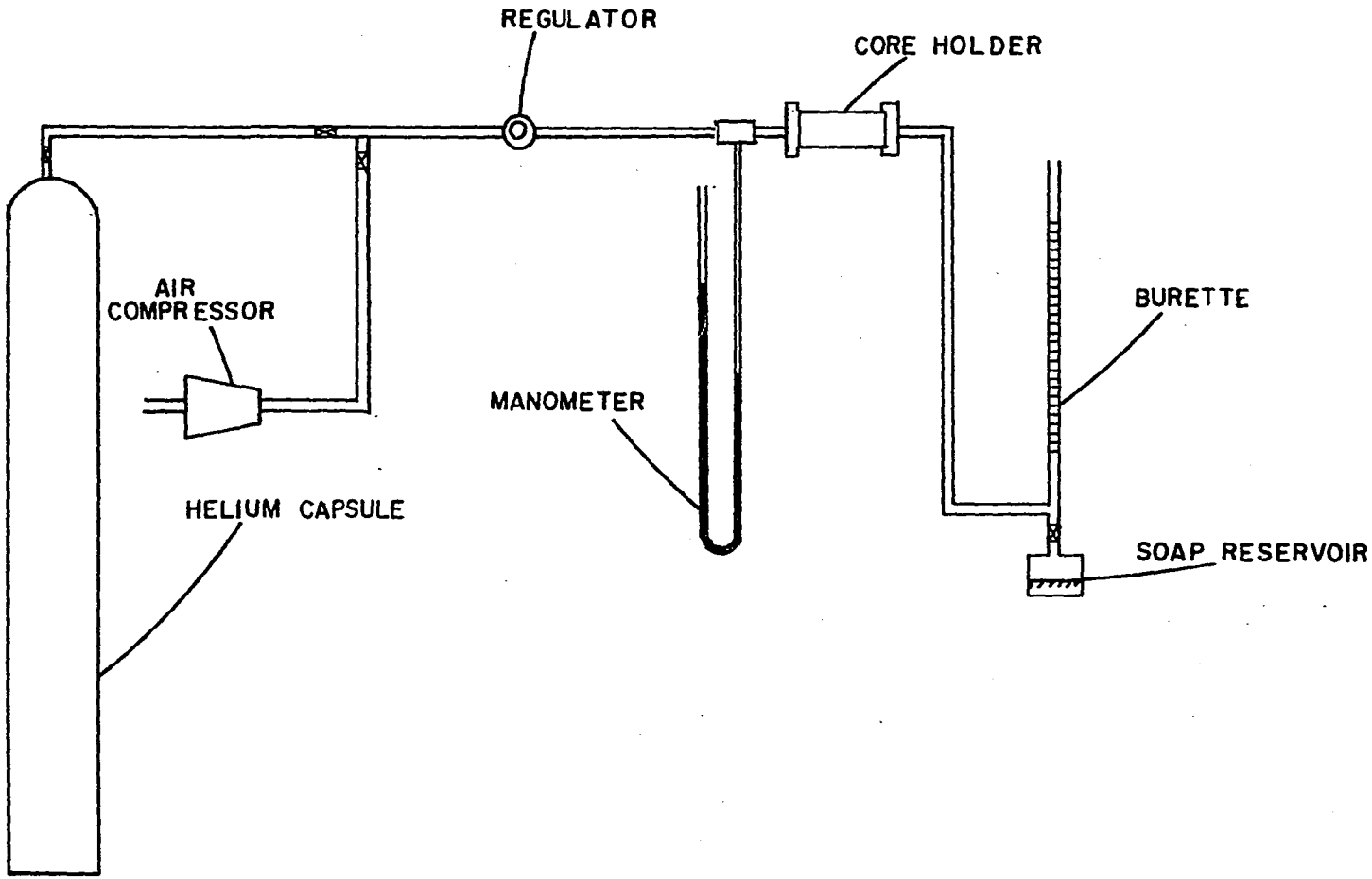


Figure 8. Schematic drawing of the apparatus used in determining air and helium flow rates.

TABLE 7

AIR AND HELIUM FLOW THROUGH SELECTED CORE PLUGS

Code Number	V-vertical H-horizontal Drilled depth	Location/ County in Oklahoma	Lithology	Air flow cc/sec	Helium flow cc/sec	Per Cent Porosity
Selected igneous and metamorphic rocks						
3	H	Dineh bi Keyah Oil Field, Apache County, Arizona	Syenite	0.000	0.000	11.5
44	V	Same as above	Syenite	0.000	0.000	9.8
29	--	----	Bytownite Gabbro	0.000	0.000	0.8
55	--	----	Gabbro	0.000	0.000	1.1
65	--	----	Syenite	0.000	0.000	0.6
45	--	----	Biotite Granite	0.000	0.000	1.2
46	ARC 13	Norfolk, Mass.	Alkali Granite	0.000	0.000	0.7
10	--	----	Pyritic Schist	0.0910	0.1021	5.5
36	--	----	Gneiss	0.000	0.000	1.6
Selected Cores from Morrow formation, N. W. Oklahoma						
34	H 4852	Beaver	Gray Calcareous Shale	0.000	0.000	1.5
57	V 4852	Beaver	Gray Calcareous Shale	0.000	0.000	1.1
22	H 10330	Blaine	Gray Calcareous Shale	0.0090	0.0097	6.8
47	H 4425	Texas	Gray Calcareous Shale	0.000	0.000	3.0

TABLE 7 (Continued)

Code Number	V-vertical H-horizontal Drilled depth	Location/ County in Oklahoma	Lithology	Air flow cc/sec	Helium flow cc/sec	Per Cent Porosity
6	H 9147	Woodward	Dark Gray Calc. Shale	0.000	0.000	3.7
25	H 9244	Woodward	Dark Gray Calc. Shale	1.0630	1.200	1.9
38	H 7777	Woodward	Gray Shale	0.1070	0.1720	10.4
48	V 9147	Woodward	Calc. Sandy Shale	0.000	0.000	1.6
50	H 9219	Woodward	Gray Shale	0.000	0.000	3.8
67	V 9219	Woodward	Gray Shale	0.000	0.000	2.4
28	H 7794	Beaver	Calcareous Sandstone	0.000	0.000	3.6
31	V 7794	Beaver	Calcareous Sandstone	0.000	0.000	4.4
70	V 7867	Beaver	Calcareous Sandstone	0.000	0.000	1.7
4	V 7010	Harper	Light Gray Sandstone	2.500	2.520	15.4
5	H 7010	Harper	Light Gray Sandstone	2.500	2.520	14.7
11	H 7000	Harper	Light Gray Sandstone	0.1842	0.1890	15.4
14	V 7000	Harper	Light Gray Sandstone	0.1175	0.1665	18.8
19	H 6959	Harper	Calcareous Shaly Sand	0.0550	0.0725	12.3
21	H 5670	Harper	Arkosic Sandstone	0.0400	0.2600	7.4
23	V 6959	Harper	Slightly Calcareous Sand	0.0202	0.0303	11.6
24	H 6946	Harper	Light Green Sandstone	0.0232	0.0286	13.9
32	H 5667	Harper	Light Gray Dense Sand	0.0001	0.0003	7.1
39	H 7010	Harper	Gray Shaly Sand	0.000	0.0001	0.3
52	V 5667	Harper	Arkosic Sandstone	0.000	0.000	7.0

TABLE 7 (Continued)

Code Number	V-vertical H-horizontal Drilled depth	Location/ County in Oklahoma	Lithology	Air flow cc/sec	Helium flow cc/sec	Per Cent Porosity
53	V 7010	Harper	Gray Shaly Sand	0.000	0.0001	1.6
56	V 6946	Harper	Light Gray Dense Sand	0.000	0.000	14.7
69	V 5670	Harper	Coarse Light Gray Sand	0.000	0.0001	7.5
1	V 6304	Texas	White Coarse Sand	1.000	1.163	17.1
7	V 4436	Texas	Light Gray Dense Sand	0.000	0.000	9.1
8	V 4444	Texas	White Coarse Sand	1.662	1.785	21.6
9	H 6314	Texas	White Coarse Sand	1.315	1.350	16.3
12	H 4422	Texas	White Coarse Sand	4.170	5.00	20.2
13	V 6314	Texas	White Coarse Sand	1.3150	1.570	16.6
15	H 4722	Texas	Light Gray Dense Sand	0.0065	0.0082	9.6
16	H 4444	Texas	White Coarse Sand	0.526	0.625	21.8
17	V 4722	Texas	White Dense Sand	0.0526	0.0650	6.9
20	V 6332	Texas	White Coarse Sand	1.665	2.000	18.6
26	H 6304	Texas	White Coarse Sand	0.735	0.860	17.5
35	H 4436	Texas	Light Gray Dense Sand	0.000	0.000	8.1
51	V 4423	Texas	White Coarse Sand	4.150	5.000	19.2
54	H 4431	Texas	White Sandstone	0.000	0.000	9.6
61	V 4431	Texas	White Sandstone	0.000	0.000	7.6
2	V 7806	Woodward	Light Green Shaly Sand	0.0111	0.0162	19.8

TABLE 7 (Continued)

Code Number	V-vertical H-horizontal Drilled Depth	Location/ County in Oklahoma	Lithology	Air flow cc/sec	Helium flow cc/sec	Per Cent Porosity
18	H 7806	Woodward	Fine Dense Sandstone	0.0238	0.0303	17.9
33	H 7835	Woodward	Fine Dense Sandstone	0.000	0.000	3.4
40	H 8668	Woodward	Fine Dense Sandstone	0.000	0.000	3.1
41	H 9199	Woodward	Light Gray Calcareous Sand	0.000	0.000	0.6
43	V 7835	Woodward	Fine Dense Sand	0.000	0.000	4.0
49	V 8667	Woodward	Fine Dense Sand	0.000	0.000	3.9
64	H 9214	Woodward	Gray Calcareous Sand	0.000	0.000	6.7
66	H 9217	Woodward	Gray Dense Sand	0.0510	0.0540	2.8
71	V 9217	Woodward	Gray Dense Sand	0.000	0.0001	4.2
42	H 7867	Beaver	Gray Shaly Limestone	0.000	0.000	1.6
37	H 6977	Harper	Gray Sandy Limestone	0.000	0.000	3.2
68	V 6977	Harper	Gray Sandy Limestone	0.000	0.0001	3.8
27	H 8633	Woodward	Dense Crystalline Limestone	0.000	0.000	0.8
58	V 8635	Woodward	Dense Crystalline Limestone	0.000	0.000	2.3
59	V 9199	Woodward	Gray Crystalline Limestone	0.000	0.000	1.2
62	V 9214	Woodward	Gray Crystalline Limestone	0.000	0.000	6.5
Selected cores from Chester Limestone, N. W. Oklahoma						
30	H 8721	Woodward	Light Dense Limestone	0.000	0.000	3.1
60	H 8721	Woodward	Light Dense Limestone	0.000	0.000	1.2
63	V 8712	Woodward	Light Dense Limestone	0.000	0.000	3.7

under pressure differential of 0.262 atmospheres, and the porosity in per cent.

The results obtained from the measurements and tabulated in Table 7 reveal that, in general, sedimentary rocks, especially sandstones, have the ability to transmit more efficiently the helium stored or entrapped in them at low pressures. The crystalline sedimentary rocks and non-fractured igneous rocks are poor conductors of helium at corresponding low pressures. Also, a plot of the helium flow rate vs the air flow rate for all the rocks studied revealed a good correlation between these two parameters studied, as shown in Figure 9. However, there was no correlation between the air and helium flow rates and the porosities of the core plugs.

Diffusional Migration of Helium

As mentioned in the previous chapters helium occurs widely in nature in very low concentrations. It is found entrapped in crystal structure, in accumulation of natural gases, ground waters, and in the earth's atmosphere. One can postulate that source of helium is a continuous process, since it is being generated constantly by radioactive decay of larger atoms. A portion of helium generated in the crust and mantle of the earth is lost to the atmosphere, and a similar portion is lost from the atmosphere into space. Little work has been done on the mode of migration of helium

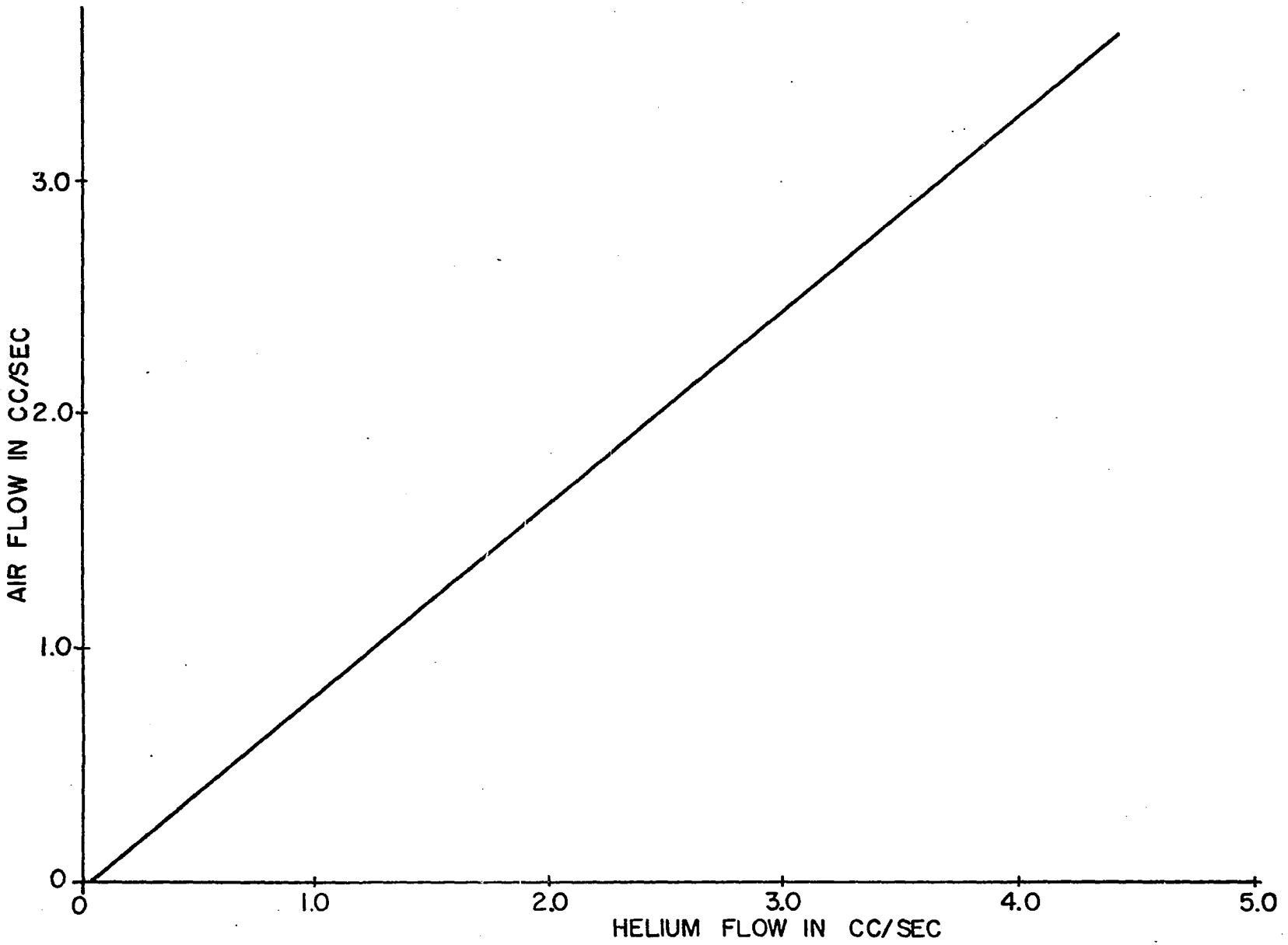


Figure 9. Helium flow in cc/sec vs air flow in cc/sec for the cores in Table 7, at a pressure differential of 0.262 atmospheres.

within the earth to the atmosphere. One purpose of this study was to examine what is the most probable means of migration through sedimentary rocks.

Due to the extreme complexities of the actual physical situations, in the following sub-sections, the helium which is generated by sedimentary rocks is neglected. The last part of this section, the actual conditions will be briefly considered.

The Physical Situation

The two actual subdivisions of crust are "sialic" or granitic, and "simatic" or basaltic layer. In this study, it is convenient to sub-divide the crustal rocks into two classes. The Precambrian rocks, which are termed "basement rocks," and the Paleozoic to Tertiary rocks, which are termed "sedimentary rocks." The above classification is one of age rather than geological nature.

Although the sedimentary rocks vary widely in character, the whole stratigraphic column may be regarded as a porous medium in which the pore size distribution varies throughout its length. The basement rocks are denser than the sediments, but nevertheless are slightly porous and fractured. Therefore the migration of helium from its sources can be considered to take place throughout a porous medium.

Migration of Helium

Helium is produced from alpha emitting nuclides, which may be in the form of crystals in the rocks or in aqueous solutions in the pores of the rocks. It is clear that the major portion of the movement of helium will take place within the pore structure in view of the disparity between the diffusivities of helium in solids and liquids. Since diffusion is the only means of mass transfer through the rock matrix, a comparison of diffusivity in a solid and in a liquid is pointed out.

Diffusivity of helium in a solid, namely silica, is of the order of 10^{-10} cm^2/sec, and for a liquid such as water is 10^{-5} cm^2/sec, (Faul, 1954). Comparing these diffusivity values shows that movement through the rock matrix represents only a minor portion of the overall movement of the helium. However, this portion of the helium movement is important as a controlling factor in the supply of helium to the pore structure. As an example, a rock subjected to tensions resulting in microfracturing has a pore structure which presents a large surface area for the escape of helium from the rock matrix. Consequently in such regions of tension the concentration of helium in the pore space may be expected to be higher than that in a similar but non-fractured area.

Within the pore spaces helium exists in two ways: as discrete bubbles alone or in association with other gases,

and in aqueous or hydrocarbon solution. Consequently there are three possible modes of helium migration: migration as bubbles, migration in solution due to fluid flow, and migration by molecular diffusion.

It is unlikely that helium moves as bubbles, because in the first place capillary action will prevent such a movement and secondly, the geometry of the pore structure would be expected to trap the bubbles. For above two reasons, such a possible mode of migration has not been considered further in the present study.

The possibility of migration of helium associated with fluid movement was studied. It is known that in some layers of sediments there is a lateral flow of ground water. This movement for the upper sediments, may have a velocity as high as hundreds of feet per year. The proportion of the helium in the pore space which is in solution, and therefore the proportion of the helium which can migrate in this manner, is dependent on the partial pressure of the helium. The total pressure in the pores is mainly fixed by the overburden pressure and therefore the partial pressure of the helium depends on the quantities of other natural gases present. As helium is the least soluble of all the natural gases it is suggested that very little of the helium which is present is actually in solution. In addition since the degree and extent of the flow of underground fluids are not

well known, it is not possible to generalize on this mode of migration.

Diffusion as a means of helium migration has been suggested by Emerson and et al (1966) to account for the variation in helium concentration with depth that he found in accumulation of natural gas. The cause of diffusion is the activational energy of each helium atom resulting in random motion. If in a given region there is a higher concentration of helium atoms than in some other region, then the random motion of the atoms will result in a mass transfer of the helium to the region of lower concentration. The rate of transfer is dependent upon the concentration gradient between the regions and the diffusion coefficient, or diffusivity, which is characteristic of the medium. Therefore, it is clear that molecular diffusion of helium does take place within the pore structure.

The Diffusivity of the Sediments

The diffusivity may be considered as a measure of the difficulty which a helium atom has in moving through the pore structure of the sediments while it is in random motion. Physically, diffusivity at a point in a porous medium is defined as the ratio between the rate of helium flux per unit area of the medium, perpendicular to the flow, and helium concentration gradient at that point. Therefore

the diffusivity can be said to be determined by two factors: the transfer medium, and the geometry of the pore structure in which the transfer medium exists. The variation of diffusivity with transfer medium depends on the chemical nature of the medium, its temperature, pressure, and also the concentration of helium in the medium. The diffusivity of a porous medium may be illustrated quantitatively by the following example: in a uniformly granular system, if the granules are spherical, the diffusivity of the system is independent of the size of the spheres. However, if the granules are disk shape, then the diffusivity varies widely with the diameter and thickness of the discs.

Simplification for Analysis

The mechanism problem of migration of helium through sedimentary rocks, as described in previous sections, is a complex problem. Some simplification is required before mathematical techniques can be applied. Up to this point, the problem has been reduced to the local migration of helium from the basement rocks as a source, through overlying uniform layers of sediments which are considered as a porous medium. The mechanism of migration which is considered the most probable is diffusion, and as a consequence of the local uniformity the lateral effects can be ignored and the problem considered to be one-dimensional.

Therefore, the problem which is to be analyzed is one-dimensional diffusion of helium from basement rocks, as the source, through overlying layers of sediments, which are the porous stratigraphic column. Every layer could be characterized by a gross or average diffusivity and the complete sediments are assumed to exist at the time origin of the diffusion process, which is the onset of sedimentation. In short it can be said that above assumptions which have been made to reduce the extremely complex problem to a simpler form. Gross uncertainties and lack of knowledge concerning so many factors, calls for the above simplifications. Finally, as stated previously, the helium generated from the sediments is ignored, and the initial concentration of helium in the sediments is zero.

Mathematical Models

From the molecular theory of gases (Hirchfelder, 1964), one could derive the diffusion equation of gases as follows: Consider a slab of rock which has the thickness of dx as shown in Figure 10. If q is the net flux or net diffusion through the slab, which is a model of a single or of several formations with uniform diffusivity, and c be the concentration of helium, one could write:

$$\frac{\partial c}{\partial t} dx = q(x) - q(x + dx) \qquad (1)$$

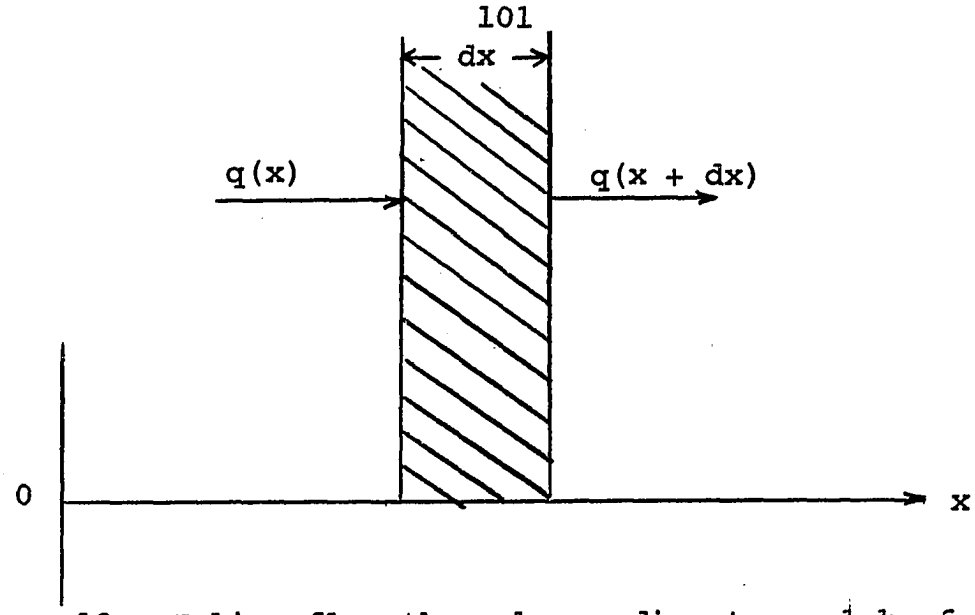


Figure 10. Helium flux through a sedimentary slab of dx thickness.

Applying Taylor expansion on the term q(x + dx),

$$q(x + dx) \cong q(x) + \frac{\partial q}{\partial x} dx \qquad (2)$$

substitution of q(x + dx) term from Equation (2) into Equation (1) will yield,

$$\frac{\partial c}{\partial t} dx = \left[q(x) - \left(q(x) + \frac{\partial q}{\partial x} dx \right) \right] \qquad (3)$$

simplifying the above equation,

$$\frac{\partial c}{\partial t} dx = - \frac{\partial q}{\partial x} dx \qquad (4)$$

But, q, the net flux or net diffusion is defined as

$$q \equiv - D \frac{\partial c}{\partial x} \tag{5}$$

Differentiating Equation (5) with respect to x

$$\frac{\partial q}{\partial x} = - D \frac{\partial^2 c}{\partial x^2} \tag{6}$$

and substituting Equation (6) into Equation (4) will yield

$$\frac{\partial c}{\partial t} dx = - D \frac{\partial^2 c}{\partial x^2} dx \tag{7}$$

cancelling the dx term from both sides of Equation (7) will give the molecular diffusion for one dimension (x-dimension) as

$$\frac{\partial c}{\partial t} = - D \frac{\partial^2 c}{\partial x^2} \tag{8}$$

Therefore the model proposed here is the general one-dimensional molecular diffusion equation of the form

$$D \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} \tag{8}$$

to which a Laplace transformation (Hirschfelder, 1964) on the variable t is applied giving

$$\frac{\partial^2 \bar{c}}{\partial x^2} = \frac{p}{D} \bar{c} = R^2 \bar{c}, \tag{9}$$

where $R^2 = \frac{p}{D}$

using the assumption made in the beginning that initial concentration of helium in the sediments is zero. Here D is the diffusion coefficient, c the concentration of helium and $\bar{c}$ its Laplace transformed formed, x is the distance from the basement, t is time, and p is the Laplace transform parameter.

Equation (9) will have solutions of the form:

$$\bar{c} = A \cosh Rx + B \sinh R x$$

where A and B are constants to be determined by the boundary conditions of the problem. These boundary conditions will take one of the following forms:

(a) $c = o$ for $t \geq o$ at some $x = x_o$

(b) $c = C_o \exp(-\beta t)$ for $t \geq o$ at some $x = x_o$.

(c) $\partial c/\partial x = o$ for $t \geq o$ at some $x = x_o$

where c is the concentration of helium which is a function of time and distance, x is the distance measured from Precambrian basement rocks, and t is the time measured from beginning of sedimentation. C_o and β determined by the abundances and decay constants of the source elements, and f_o is also determined by abundances of the source elements and their decay constants.

Since the extent of sedimentary layers, their physical characters such as grain size and grain shape, homogeneity, rock type, porosity, permeability, and diffusivities that are quite different, no attempt is made to further consider this diffusional problem. Moreover, the form of the boundary conditions in specific regions are essentially unknown. Also, some local conditions such as temperature and pressure gradients which directly affect the diffusion rates, are highly variable factors.

In addition to that generated in basement rocks, if one considers the helium generated by the sediments Equation (8) becomes

$$D \frac{\partial^2 c}{\partial x^2} + C_p = \frac{\partial c}{\partial t}$$

Where: $c = f_1 (x,t)$

$C_p = f_2 (x,t)$

Where c is the concentration at any point due to the helium generated from igneous rocks and C_p is the helium derived from sedimentary rocks. Needless to say the effects of temperature and pressure were neglected in the analysis of diffusional migration.

In conclusion helium migration through sedimentary rocks is an extremely complex problem. Other modes of migration may be operational, but the diffusional migration is

the most probable one. One other means of migration is by fluids, as discussed in Chapter V, which is of considerable importance because of the mobility of the underground fluids.

CHAPTER VIII

ACCUMULATION OR ENTRAPMENT OF HELIUM

The alpha particles produced in the radioactive disintegration processes are basically helium atoms. After the loss of its original energy, each alpha particle will behave as an atom of helium gas, being principally occluded in the interstices of the rock minerals. There will tend to be an evolution of helium from the rock particle surface in the course of geologic time, due to metamorphism and faulting, and the mobil gas will migrate upward whenever channels of permeability are afforded by the stratigraphic circumstances.

The concept that helium in the petroleum gases is derived from relatively shallow igneous rocks containing high proportions of uranium and thorium minerals (See Chapter I) is not always borne out. Although in many areas helium and nitrogen gases occur in reservoirs relatively close to basement rocks, e.g., the buried granite ridge of the Nemaha Mountains, in other areas such as southeastern Kansas, the gas from shallow zones contain a larger percentage of helium than that from deeper strata. This may,

of course, be due to local migration but in general, there is no universally clear correlation between the helium content and local radioactivity. However, it has been suggested that the large volume of helium in the Panhandle gases of Texas and Oklahoma is due to the occurrence of radioactive petroleum residual deposits in that neighborhood (Pierce et al, 1964). Moreover when deeply buried rocks become heated, as they evidently have been in some localities during certain geological epochs, helium would have a particular and special tendency to escape at one stage of the heating. If then the helium were collected and trapped by overlying impermeable barriers in a cooler environment, there would be a helium rich gas.

Ability to Hold Helium

From the flow rate studies in the previous sections of this chapter, and Table 7, it is apparent that the ability to hold helium varies for different rock types. Study of Table 7 points out that shales, and cap rocks are the most impermeable of rock types to helium and therefore are the best helium holders. Also, crystalline limestone, anhydrite, and non-fractured igneous rocks have the ability to retain helium in themselves. The fact that natural gases rich in helium generally are present in Paleozoic rocks relatively close to basement rocks, indicates that at least some helium derived from basement rocks was diffused vertically and

locally trapped in these geologically impermeable beds. These rocks are highly compacted and act as a seal to prevent the flow of helium from the structural traps. The seal that acts as an impermeable cover may also be oil or oil-water as well as some rocks mentioned previously. Of course, the accumulation of high percentages of helium requires considerable time, and high helium contents are associated more often with natural gases from the older geological formations.

Effect of Radiation Damage

From the studies by Faul (1954) and Funkhouser (1968) on helium loss and retentivity, one can assume that the rate of helium escape is in proportion to the damage of molecular structure and the amount of helium present. Most of the radiogenic helium present is produced mainly on grain boundaries and is consequently diffusible. The emission of the alpha particles which subsequently produce helium atoms, causes structural and mechanical damage of the molecular lattice of the alpha emitter. One can conclude that the radiogenic gases such as helium and argon are trapped in these lattice defects caused by radiation damage.

Conditions Favoring Helium Accumulation

Rogers (1921) in his classic work emphasized the fact that helium was most likely to be found at shallow

depths. However, Silurian gas in Vinton County, Ohio, contains a greater quantity of helium than does gas from Mississippian beds at the same locality (Beebe, 1968). At Pinta Dome field Arizona, the deeper zone (1032 ft) contains gas with an 8.09 per cent helium content, but the shallower zone (780 ft) contains 6.98 per cent. Recent data from Keyes field in Oklahoma, Hatcher field in Colorado, and other localities, seem to contradict the above conclusion. A chart prepared by Pierce and et al (1955) clearly points out that the helium content of natural gases increases with the age of the gas producing reservoir. Although it is impossible to develop a generalized relation between optimum age and geologic conditions necessary for helium concentration, the following conclusions may be proposed:

(1) Helium accumulations may be found in the stratas of any geologic age, but it appears to be most concentrated in the Paleozoic rocks, where presumably the disintegration of radioactive elements has been progressing for longer periods of time than in younger strata.

(2) Helium accumulation need not be restricted to shallow depths. However because the diffusive qualities of helium increases with increasing pressure and temperature, it may be that the efficiencey of the seal over the helium-containing reservoir must increase in proportion with depth

to some critical point. At this point even the most efficient sedimentary-rock seal is not able to prevent the diffusion of helium.

Retentivity and Diffusivity of Rocks

Some common rock-forming minerals do not retain all the helium generated in their structures during their geological history. According to Goldschmidt (1954), the retentivity of feldspar is low, whereas minerals with close-packed structures, such as magnetite, pyroxenes, and amphiboles, appear to retain helium. The size of the helium atom is large compared with the vacant spaces in the molecular structural configurations of minerals which retain helium better than others. If in the lattice, the volume of the space unoccupied by ions is large, the diffusion of helium in such lattice takes place more rapidly than in the lattices with a closepack structure. This selective retention and loss are the causes of variable helium content in rocks and minerals.

Any "excess" helium is that which cannot be explained by accumulation during the decay of the known radioactive elements. "Excess" helium and other rare gases (Argon) in minerals such as beryl (Damon and Kulp, 1958) are probably due to presence of helium in magmatic gases at the immediate environment of crystallization and is in the form of inclusions. This "excess" amount could not have been derived

from selective retention of helium in beryl. This property is more common among high temperature minerals derived from magma.

CHAPTER IX

NATURAL GAS ANALYSES

Most of the chemical analyses of natural gases of the United States are carried out by the U. S. Bureau of Mines. Results of these analyses are published by the Bureau in Information Circulars (IC), Report of Investigations (RI), and Bulletins (B). In addition to U. S. Bureau of Mines, several authors (27, 31, 71) have analyzed natural gases and have reported their composition in mole per cent of components, i.e., methane, ethane, propane, nitrogen, helium and argon content.

The purpose of this chapter is to investigate and analyze the relationship(s) between the abundances of helium and argon (a radiogenic gas) in natural gases of different composition, environment and age. Composition of helium-rich gases has been found to be quite variable, although in some gas fields a correlation has been suggested between helium and nitrogen content. To examine this variability, a variety of natural gases covering a wide compositional and environmental range have been considered. Forty natural gas samples were taken from Zartman's work (1961) and were

examined for their helium and argon content. The results of this examination are presented in Table 8 with pertinent information for each sample.

The natural gases contained amounts of nitrogen varying from 0.1 to 42.5 per cent. The origin of nitrogen in natural gases has been explained in terms of: (1) the introduction of atmospheric nitrogen; (2) the release of nitrogen by bacterial decomposition of nitrogen compounds; (3) the release of nitrogen by the inorganic chemical breakdown of organic compounds; and (4) the liberation of inorganic (possible radiogenic) nitrogen from igneous rocks.

Helium-Argon Ratio

If essentially all of the helium contained in natural gases is produced by radioactive disintegration of uranium and thorium, and the radiogenic fraction of argon produced by the electron capture decay of potassium, one could make certain theoretical calculations to determine the values to be expected for the radiogenic helium and argon abundances and their ratio. In order to know the abundances of helium and argon observed in natural gases it is necessary to consider variation of helium and argon production with time, natural distribution of uraniu, thorium and potassium in rocks and the process of gas migration and accumulation into gas reservoirs.

A number of gas transport mechanisms could also produce a fractionation of argon and helium. If during

TABLE 8

NATURAL GAS ANALYSES FROM DIFFERENT LOCALITIES

No.	State	County	Depth in ft to Producing Horizon	Geologic System	N_2%	He ppm	A ppm	Producing Zone's Lithology
1	California	Glenn	3400	Cret.	1.6	47.5	57.4	ss
2	California	Sacramento	4100	Eocene	1.57	41.2	52.2	ss
3	California	Sacramento	5400	Eocene	0.86	37	67	ss
4	California	San Joaquin	2340	Eocene	30.97	96.6	140	ss
5	California	San Joaquin	2500	Eocene	3.76	101	88.2	ss
6	California	Sutter	5400	Cret.	9.15	37.6	53.1	ss
7	California	Yolo	2500	Eocene	2.65	85	125	ss
8	Colorado	Moffat	8075	Paleocene	4.03	101	32	ss
9	Colorado	Moffat	4885	Paleocene	2.40	63	39	ss
10	Colorado	Moffat	2851	Eocene	2.30	140	118	ss
11	Colorado	Wallace	5006	Penn.	36.6	26000	1400	ss
12	Louisiana	Webster Parish	8554	Jur.	1.0	152	26.5	ss
13	Louisiana	Webster Parish	9174	Jur.	0.87	151	42.0	ss
14	Michigan	Hillsadle	3755	Ordo.	22.2	1350	360	lm
15	Mississippi	Forest	7303	Cret.	1.48	359	81.9	ss
16	New Mexico	Harding	2075	Perm.	0.12	44.5	28.0	sh + ss
17	New Mexico	Harding	2074	Perm.	0.15	46.6	29.2	sh + ss
18	New Mexico	Lea	5330	Perm.	1.98	348	57.3	ss
19	New Mexico	Lea	6420	Perm.	2.6	480	66.8	ss
20	New Mexico	Lea	3900	Perm.	3.4	69.4	117	lm
21	New Mexico	Rio Arriba	2630	Cret.	0.94	172	46.1	ss
22	New Mexico	San Juan	6366	Penn.	42.5	62200	5630	lm

TABLE 8 (Continued)

No.	State	County	Depth in ft to Producing Horizon	Geologic System	N_2%	He ppm	A ppm	Producing Zone's Lithology
23	New York	Eri	3011	Silur.	5.6	1640	77.1	ss
24	Oklahoma	Cimarron	4628	Penn.	24.9	22600	1080	ss
25	Pennsylvania	Cameron	6627	Dev.	0.50	203	6.8	ss
26	Pennsylvania	Mercer	590	Miss.	1.9	1575	35.8	ss
27	Pennsylvania	Venango	1902	Dev.	0.64	805	14.9	ss
28	Texas	Coke	5200	Penn.	6.5	1720	376	ss + lm
29	Texas	Crocket	8200	Penn.	2.5	593	117	lm(reef)
30	Texas	Hartley	3200	Perm.	16.6	9370	877	dolo
31	Texas	Moore	2560	Perm.	8.95	4180	470	dolo
32	Texas	Moore	3525	Perm.	9.70	4480	482	dolo
33	Texas	Moore	3000	Perm.	9.6	4170	461	dolo
34	Texas	Moore	3000	Perm.	15.2	7000	710	dolo
35	Utah	Carbon	3100	Perm.	0.60	232	79.5	ss
36	Utah	Carbon	3100	Perm.	0.55	187	65.4	ss
37	Wyoming	Sweetwater	5400	Cret.	2.08	75	27	ss
38	Wyoming	Sweetwater	2375	Eocene	1.22	158	73.4	ss
39	Wyoming	Sweetwater	2605	Cret.	1.80	757	66.8	ss
40	Wyoming	Uinta	2768	Cret.	3.09	152	17.5	ss

the time of gas accumulation, the helium and argon are transported by solution in connate water, fresh water, or in petroleum the He/A ratio will be influenced by the relative solubilities of these gases in the transporting medium. Since the solubilities of argon and helium in crude oil are unknown in this important transmitting medium, the following section will elucidate on helium and crude oil solutions. Moreover, argon is not considered here because this study is mainly pertinent to helium and only traces of argon have been reported from Northwestern Oklahoma.

Helium-Crude Oil Solution

The experiment was carried out in a PVT cell located at the University of Oklahoma, School of Petroleum and Geological Engineering laboratories. A crude oil of 37.5° API gravity was chosen, and the cell was under pressure up to 45000 psi, at the room temperature of 78°F.

The purpose of this investigation was to study the mechanism by which a gas is dissolved by a liquid. In particular, the report is concerned with the solution of helium in crude oil. To understand the method by which a gas is dissolved in liquid, it is necessary to study the concept of vapor pressure of a solution. An interesting kinetic-molecular description of the way in which the equilibrium vapor pressure is established can be given (Barrow, 1966). In this view, equilibrium is described as the

balancing of the rate of evaporation with the rate of condensation.

At any temperature, as the result of thermal jostling, some molecules will acquire enough energy to overcome the attractive forces of neighboring molecules and will break away from the liquid. At the same temperature there will be continual collisions of vapor molecules with the liquid surface. A fraction of these colliding molecules will have so little kinetic energy that they will be unable to pull away from the attractive forces of the liquid molecules. These opposing processes of evaporation and condensation reach an equilibrium state which is characterized by the equilibrium vapor pressure.

Therefore, the vapor pressure is a function of the kinetic energy of the molecules in question and of the attractive forces which exist between the molecules. The system here which is of concern, is an oil reservoir, and is so thermal that any consideration of the kinetic energy of the molecules can be omitted and attention can be focused on the intermolecular forces of attraction.

Four types of contributions to intermolecular attractions can be recognized in ordinary liquids (Barrow, 1966). These are dipole-dipole attraction, the induction effect, London dispersion forces and hydrogen bonding. The first two require the molecule to exhibit a dipole moment. The

last force of attraction requires the molecule to contain hydrogen with a partial positive charge, or an electron-rich atom as the result of bonding. Since Helium neither exhibits a dipole moment nor is it electron-rich, these three forces are absent. The London dispersion forces result from instantaneous dipole moments and are extremely weak in the case of helium. Consequently, the intermolecular forces of attraction on helium are very weak and it has little tendency to condense at reservoir temperatures. As a result helium's vapor pressure is very high, abnormally so. Crude oil, on the other hand, contains many dipole moments and much hydrogen bonding which causes its vapor pressure to be much less than that of helium.

Nest it is important to consider the theory and results of the dependence of the relative liquid composition on the component vapor pressures. Ideal gases are found to conform to an ideal relation expressed by Dalton's Law which states "The total pressure of a mixture of ideal gases is equal to the sum of the pressures of the components." Since liquids exist only because of molecular interactions, no such ideal liquid solutions can be expected in the same sense as an ideal-gas solution. Some solutions behave in a simple enough manner, however, to warrant the use of the term "ideal solution." Such solutions obey Raoult's Law which states "The solution of gas within a

liquid is directly proportional to the pressure exerted by the gas above the liquid." This linear relation can be expressed as:

$$P_a = x_a P^o_a \tag{1}$$

where P_a and P_b are the vapor pressure of a and b above a solution of mole fraction x_a and x_b, and the vapor pressures of the pure components are P^o_a and P^o_b.

Since the partial pressure of a gas is proportional to the number of moles of the gas per unit volume, the mole fractions of the vapor can be written as:

$$x_a\ (\text{vap.}) = \frac{P_a}{P_a + P_b} \quad \text{and} \quad x_b\ (\text{vap.}) = \frac{P_b}{P_a + P_b} \tag{2}$$

or:

$$x_a(\text{vap.}) = \frac{x_a P^o_a}{P_a + P_b} \quad \text{and} \quad x_b(\text{vap.}) = \frac{x_b P^o_b}{P_a + P_b} \tag{3}$$

The ratio of the mole fractions of the vapor components in the liquid is therefore given as:

$$\frac{x_a\ (\text{liq.})}{x_b\ (\text{liq.})} = \frac{x_a\ (\text{vap.})\ P^o_b}{x_b\ (\text{vap.})\ P^o_a} \tag{4}$$

This expression can be used to calculate the composition of an ideal solution in equilibrium with a vapor of any composition. The qualitative result which should be noted is

that the liquid will be relatively richer in a if P^{o}_{a} is less than P^{o}_{b}; that is, if a is less volatile than b.

From the expression in equation (4) and the knowledge that the vapor pressure of pure helium is much greater than that of crude oil, it is obvious that very little of helium is in the liquid state, or:

$$\frac{x_{He(liq.)}}{x_{oil\ (liq.)}} = \frac{x_{He\ (vap.)}\ P^{o}_{oil}}{x_{oil\ (vap.)} P^{o}_{He}} \qquad (5)$$

Using the realistic vapor pressures of 10 psi for crude oil and infinite psi for helium (since helium is above its critical temperature at reservoir conditions) one could see that the ratio of helium to crude oil is infinitely greater in the vapor phase than in the liquid phase:

$$\frac{\infty}{10} \frac{(x_{He})}{(x_{oil})_{liq.}} = \frac{(x_{He})}{(x_{oil})_{vap.}} \qquad (6)$$

Consequently, no helium will go into solution with crude oil in the reservoir.

Noble Gas Abundances in Natural Gases

The helium content of the gas samples examined varies between 37 ppm and 62200 ppm (1 ppm = 10^{-4} per cent) and the radiogenic argon content varies between 6.8 and 5630 ppm. Since any attempt to explain the occurrence of

the rare gases in natural gases must account for the absolute amounts and concentrations as well as for the ratio of radiogenic helium to argon, factors affecting these abundances will now be discussed.

Whereas the He/A ratio is only slightly time dependent when considered over times comparable to the age of the earth, the actual production of these gases is strongly time-dependent. The radiogenic helium and argon content of a natural gas reservoir is not necessarily proportional to the age of the source rock, but is, rather, a complicated function of the accumulation history of the gas. It is possible that much of the radiogenic gases are incorporated into the natural gases by a sweeping-up effect during the time of migration from source to the reservoir rock (Zartman, et al, 1961). In such an event, the He and A content of the rocks at the time that they were traversed by the accumulating gases would be an important factor. The sweeping effect of liquids such as connate water and petroleum could also partially dissolve the uranium, thorium, and potassium of the rocks through which fluids are migrating. After following the entrapment of these fluids, due to their insoluble nature, helium and probably argon escape out of the solution and will enter into the gas cap which lies directly above the entrapped petroleum. However, if there were little helium or argon to escape before gas migration, the length of time between rock induration

formation, and petroleum accumulation would determine the concentration of He and A in the pore space. Studies of a number of oil and gas fields (Leverson, 1967) have indicated that this time between source rock deposition and petroleum migration may vary up to hundreds of millions of years.

Helium Distribution in Natural Gas

More than 4000 natural gases analyses reported by the U. S. Bureau of Mines include data on helium. These gases come from a wide variety of geological occurrences. Because of the large number of analyses, it is possible to obtain a significant frequency curve. Zartman, et al (1961) used 3000 analyses of the samples containing less than 0.8 per cent helium. Because an excessive number of samples that were analyzed were from helium producing areas, all analyses reporting over 0.8 per cent helium were discarded. of the total number of gas analyses, 3 per cent contained helium in concentration of over 0.8 per cent. This 3 per cent fraction of the annual gas production has an average helium content of 1.5 per cent (Miller, 1965). The following values were determined for the statistical analysis of selected natural gases mentioned previously:

Mean = 0.2170 per cent σ = Standard deviation = 1.59

Median = 0.0610 per cent μ = Mean of original population = 2.80

Mode = 0.0049 per cent

Figure 11 illustrates the frequency curve and uses these parameters for the frequency function:

$$\frac{d\Lambda(x)}{dx} = \frac{1}{2\pi\sigma x} \exp - \frac{(\ln x - \mu)}{\sqrt{2\sigma}}^2$$

This curve may be compared with the histogram which is unimodal in character and x is the helium per cent of the natural gas. From this observation one can conclude that the high helium content does not, in a statistical sense, represent low-probability events on the tail of a continuous-probability curve. Therefore, one could generally state that the helium, argon and other radiogenic gases in natural gas have been obtained from rather average rock type. The variation in abundance of radiogenic helium and argon in the gases studied are probably due to the effect of leakage and entrapment, solubility, porosity and age of the source rocks. However major differences in the abundances of helium may be due to large variations in the abundances of uranium, thorium, and alpha emitting fluids in the source rocks.

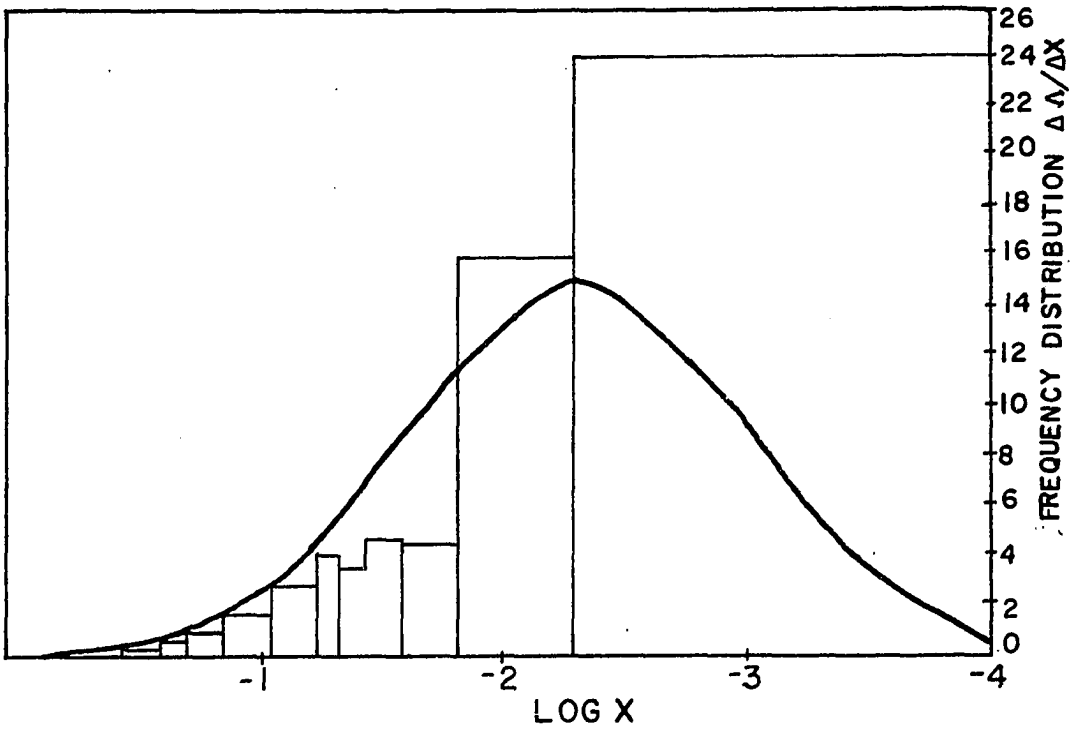


Figure 11. Frequency curve and histogram showing the distribution of helium in natural gas.

CHAPTER X

CONCLUSIONS

The following conclusions have been drawn from this study of generation, migration, distribution, and entrapment of helium:

1. The uranium concentration (percent) of all the major rock types and certain fluids has been determined by using a 400-Channel Pulse Height Analyzer. By knowing the quantity of uranium in any sample, the amount of helium generated by that sample can be estimated.

2. Although elements like radium and polonium are also alpha emitters, as well as uranium and thorium, their abundance is relatively much smaller than uranium and thorium. Since uranium to thorium ratios are documented in literature, only uranium was considered.

3. Thorium to uranium ratio of 3 to 1 is pointed out in earlier parts of this work. Considering the generation rates of helium from these two elements, one can conclude that thorium has almost an equal potential to generate helium as does uranium.

4. Uranium content of the sedimentary rocks examined (Table 4) indicates that these rocks are potential helium generators.

5. In igneous and metamorphic rocks, radioactivity due to uranium and thorium stems from the accessory minerals. However, the sedimentary rocks obtain their radioactivity mainly from the cementing materials and asphaltic content.

6. The alpha emitters such as uranium, thorium, and radium have the ability to migrate.

7. The radioactivity of igneous rocks increases from low values in the basic types through intermediate to the acidic types for the high values. Sedimentary rocks have radioactive content increasing from limestone (least radioactive) to sandstones, shales, and clays (most radioactive).

8. Helium accumulations are generally found in the stratas of any geologic age, with no restriction on depth, or concentration of alpha emitters.

9. The wide variation in helium content of many natural gases is due to a combination of variations of many factors which govern its production, entrapment, and escape. These variations are: the local concentration of alpha emitters, selective retentivity, diffusivity, migration passages, and age of the host rock. Moreover, variation in abundance of radiogenic helium and argon are due to the effects of leakage, porosity, and solubility.

10. In case of equality of conditions such as the concentration of alpha emitters, retentivity, diffusivity, etc., the helium content is greater in older rocks than the younger rocks. On the other hand radioactive concentrations are higher for younger rocks than the older ones.

11. Natural gases rich in helium are generally rich in nitrogen and argon. The ratio of helium to argon in gas analyses studied suggests that these two gases are from radiogenic origin. The good correlation existing between helium and argon is probably the best indication that these gases are from radiogenic origin. However, the correlation is not so well defined for nitrogen as for argon.

12. There is no universal and clear correlation between helium content and local radioactivity. Nevertheless, the helium in most of the natural gas deposits has been derived from the alpha emitters within or surrounding the host rocks.

13. Examination of the samples from Dineh bi Keyah oil field, Apache County, Arizona, indicates a relatively high radiation activity. Its impermeability to helium, and its high uranium content, could be correlated with the high helium content (6.2 percent) of the natural gas obtained from that field.

14. The flow rate studies of different rock types indicated that shales and caprocks are the best seals to retain helium.

15. The most probable mode of migration of helium is molecular diffusion from the rock matrix. Also, ground water fluids, connate water, and petroleum have the ability to transport helium.

16. Joints and fractures, up to a size of a major fault, are possible transmitting channels of helium generated from deeper basement rocks to overlying or adjacent rocks.

17. Although the solubility of uranium and thorium are low in petroleum and brines, a favorable solubility factor could account for extremely high helium contents (8 mole percent), by producing a fluid which is highly radioactive.

18. Subsequent migration of petroleum and brines into traps causes the transportation of certain radioactive minerals in these fluids. Upon entrapment of such fluids helium will evolve from the solution due to its very insoluble nature, and will be trapped in overlying gas caps.

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APPENDIX

Calculation of 1/M Proportionality Constant

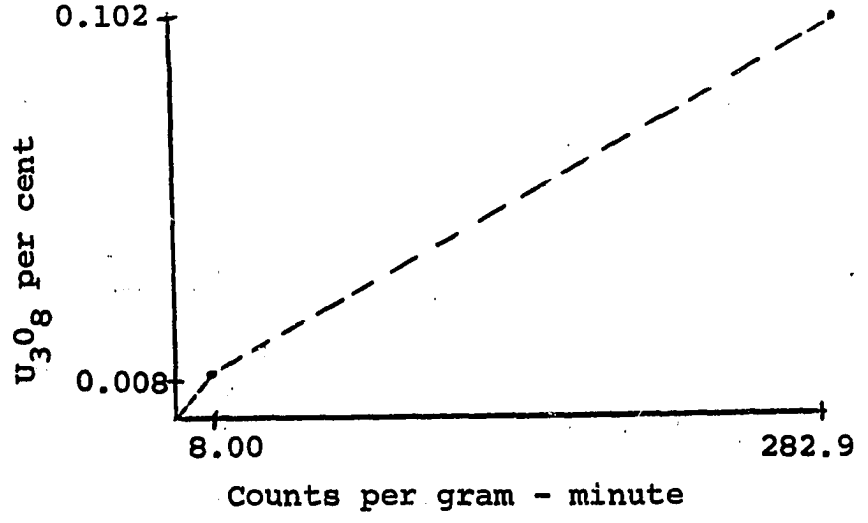
The proportionality constant of 1/M is used to convert the Specific Radiation Activity in counts per gram-minute to U_3O_8 per cent. The uranium per cent could also be calculated by multiplication of 0.867 times the U_3O_8 per cent. The following is the procedure to calculate U_3O_8 and uranium percentages:

Known Values:

Point 1: 8.00273 counts/gram-minute from 0.008% U_3O_8 sample.

Point 2: 282.95517 counts/gram-minute from 0.102% U_3O_8 sample.

From the basic law of radiation, $-dN/dt = \lambda N$, and the assumption that linear relationship exists between points one and two, and that these points are collinear with the origin (0.0, 0.0) on a plot of counts per gram-minute vs. U_3O_8%, one could draw the following graph:



The slope of the line in the above graph could be simply estimated by knowing the two points on the line:

$$\text{Slope} = (0.102 - 0.008)/(282.95344 - 8.00273)$$
$$= (0.94)/274.953 = 3.418760 \times 10^{-4}$$

Then the slope of the line is the proportionality constant or 1/M, and $U_3O_8\% = 1/M$ (Counts/gram - minute.

Therefore,

$$U_3O_8\% = (3.418760 \times 10^{-4}) \times (\text{Counts/gram - minute})$$

Since the uranium per cent, by weight is

$$U\% = (0.867)(U_3O_8\%)$$

$$U\% = (0.867) \times (3.418760 \times 10^{-4}) \times (\text{Counts/gram-minute})$$

or

$$U\% = (2.96397 \times 10^{-4}) \times (\text{Counts/gram - minute})$$

This constant of 2.96397×10^{-4} is the value of 1/M used in the uranium per cents in Tables 3, 4, 5, and 6.

Sample Calculation of Specific Radiation Activity

Calculation of the specific radiation activity caused only by the uranium content of the sample ARC No. 13, Alkali Granite from Norfolk County, Massachusetts, is considered here. The Specific Radiation Activity and uranium per cent of this sample could be found in Table 3. The results of net radiation counted in each channel, and the graph of total net gamma ray counts recorded in each of the 200 channels, are illustrated in Figures 5 and 4, respectively. Only one peak will be taken to show how to calculate the

specific radiation activity. In our calculations all the peaks between Channels 33 and 44 were considered to obtain the representative radiation due to uranium of the sample. As an example, consider the peak in Channel 35 in Figure 5.

The Specific Activity for each peak is given by the following equation:

$$S.\ A. = \frac{(\Sigma C_i) - (\text{No. of Ch.})(\frac{LCO - RCO}{2})}{(\text{Time})(\text{Weight})}$$

where: ΣC_i = The summation of all the counts in the channels of interest from left cut-off to right cut-off, inclusive.

No. of Ch. = The actual number of channels considered for each peak, from left cut-off to right cut-off, inclusive.

LCO = The number of counts recorded in the channel which is used as the Left Cut-Off.

RCO = The number of counts recorded in the channel which is used as the right Cut-Off.

Time = The time which the sample was counted, in minutes.

Weight = The weight of the sample in grams.

Therefore, one could calculate the Specific Activity (SRA) for the Channel 35 of Figure 5 as the following:

$$S.\ A. = \frac{(90 + 208 + 151 + 134 + 93) - 5\ (\frac{90 + 93}{2})}{(40)(50)}$$

$$S.\ A. = \frac{676 - 547}{2000} = \frac{219}{2000} = 0.1095$$

S. A. = SRA = 0.1095 Counts/gram-minute, for Channel 35.